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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

THE STRONTIUM – ANTIMONY SYSTEM AND THE HEATS OF FORMATION OF COMPOUNDS OF STRONTIUM AND ANTIMONY

S. A. Shchukarev, M. P. Morozova and Kan Kho-in

As far as we are aware, there is no reference in the literature to the strontium-antimony system. In the present work this system was studied by determining the density of melts of different composition and constructing, on the basis of the data obtained, the relationship between the gram-formula volume and the composition, by examining microsections, by constructing the cooling curves for several antimony-rich melts, and by determining the heats of reaction of melts of different composition with dilute hydrochloric acid.

The starting materials for the preparation of the melts were metallic strontium, prepared by a high-vacuum aluminothermic process, and antimony (analytically pure). The melts rich in antimony were prepared by fusing the components in quartz test dishes, while the melts rich in strontium were prepared in hermetically sealed steel crucibles. All the operations with the melts were carried out in a special chamber in an atmosphere of dry carbon dioxide. The density of the melts was determined in a vacuum pyknometer using thoroughly purified and dehydrated paraffin as sealing liquid.

Table 1 gives the results of the determination of the density of melts of different composition and the gram-formula volumes calculated on the basis of this value.

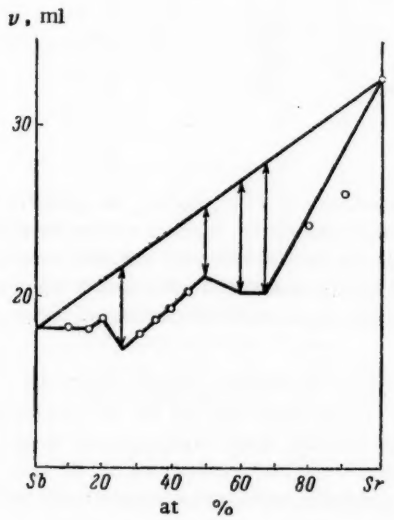

Fig. 1. The relationship between the gram-formula volumes and composition in the Sr–Sb system (the arrows indicate the magnitudes of the contraction taking place on compound formation from the elementary substances).

From Figure 1, which shows the change in the gram-formula volumes as a function of the composition, it is readily seen that there are special points on the curve corresponding to strontium contents of 15, 20, 25, 50, 60 and 67 at. %. Cooling curves were constructed for four melts. The results of these experiments are given in Table 2.

It is evident that the eutectic nearest to the antimony corner lies close to 20 at. % strontium. We did not establish accurately the composition of the eutectic since the purpose of the work was only to establish the composition of the stable compounds in this system. The part of the liquidus curve shown in Figure 2 does not confirm the existence of the compounds indicated by the gram-formula volume curve (Fig. 1). In a study of the Sr–Bi system [1] we were able to establish full agreement between the results of thermal analysis and pyknometric measurements. In the present case there is obvious disagreement. It appears to us that the breaks on the gram-formula volume curve, which are not confirmed by the liquidus curve, are explained by the special properties of the eutectic. The particular crystallization conditions close to the eutectic melts may also be responsible for the somewhat unexpected values obtained for their densities. In the case of the

TABLE 1

Sr content (at. %)	Gram-formula weight	Density at 20° (g/cc)	Mean value for the density	Values for the gram-formula volumes (in cc) at 20°	Mean value for the gram-formula volumes
10	118.35	6.45, 6.48	6.47	18.4, 18.3	18.3
15	116.64	6.36, 6.32	6.34	18.3, 18.5	18.4
20	114.93	6.07, 6.09	6.08	18.9, 18.8	18.9
25	113.26	6.63, 6.67	6.65	17.1, 16.9	17.0
30	111.52	6.18, 6.20	6.19	18.0, 17.9	18.0
35	109.82	5.87	5.87	18.7	18.7
40	108.11	5.61, 5.63	5.62	19.3, 19.3	19.3
45	106.40	5.21	5.21	20.42	20.42
50	104.70	4.86, 4.84	4.85	21.5, 21.6	21.6
60	101.28	4.88, 4.88	4.88	20.8, 20.8	20.8
67	98.90	4.79, 4.82	4.80	20.5, 20.4	20.5
70	97.87	4.59, 4.49	4.54	21.3, 21.7	21.5
80	94.46	3.85, 3.86	3.86	24.5, 24.4	24.5
90	91.03	3.41, 3.42	3.42	26.6, 26.7	26.7

TABLE 2

Sr content (in at. %)	Temperature of onset of crystallization	Temperature of eutectic halt	Duration of eutectic halt (in seconds)
5	625°	598°	120
10	616.4	602	270
15	608	596.8	390
20	603	—	570

Sr–Bi system the strontium content in the Sr–$SrBi_3$ eutectic amounts to 15 at. %, i.e., the quantity of melt components crystallizing simultaneously at Sr contents of 10 at. % and above is small and has no effect on the shape of the "gram-formula volume–composition" curve. In the Sr–Sb system the eutectic contains approximately 20 at. % strontium. Consequently, in this case the eutectic makes up a considerable fraction of the melts containing 10, 15, 20 at. % strontium, as a result of which its particular properties are shown more sharply.

The microsections of the melts containing 1.5, 2, 5, 10, 15, 20 at. % strontium showed clearly the gradual increase in the area occupied by the eutectic. The sections of the melts with 25, 50, 60 and 67 at. % strontium showed no signs of the crystallization of two phases. On the other hand, crystals of one phase interspersed with another were fairly readily observed on the sections of the melts containing 30, 40 and 55 at. % strontium. The sections of melts with strontium contents greater than 70 at. % showed clearly the columnar crystals of metallic strontium.

Thus it is possible to state that in the Sr–Sb system there exist four compounds: $SrSb_3$, Sr Sb, Sr_3Sb_2 and Sr_2Sb, i.e. the same compounds were established some time ago for the Sr–Bi system. The Sr–Sb system apparently resembles the Ca–Sb system, at any rate in the region of high antimony content. Indeed, Dolski [2] has established that a eutectic of calcium and an unknown phase lies at 22 at. % calcium.

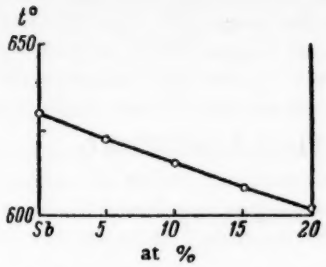

Fig. 2. Part of the liquidus curve for the Sr–Sb system.

We determined the enthalpies of formation of some of the compounds formed by strontium and antimony from the enthalpies of their reaction with normal hydrochloric acid solution. The method for carrying out the calorimetric determination has been described by us earlier [3].

$$SrSb_{кр.} + 2HCl_{р-р} = SrCl_{2\ р-р} + Sb_{кр.ч} + H_{2\ газ}$$

$$Sr_3Sb_{2\ кр.} + 6HCl_{р-р} = 3SrCl_{2\ р-р} + 2Sb_{кр.} + 3H_{2\ газ}$$

$$Sr_2Sb_{кр.} + 4HCl_{р-р} = 2SrCl_{2\ р-р} + Sb_{кр.} + 2H_{2\ газ}$$

The enthalpy changes found for the given equations were equal to 83.82 ± 2.3, 255.03 ± 1.2, 182.79 ± 1.1 kcal per gram-formula respectively. Using the known values of the enthalpies of formation and solution of hydrogen chloride and strontium chloride, these values make it possible to calculate the enthalpies of formation of the compounds of strontium and antimony studied.

$$Sr_{кр.} + Sb_{кр.ч} = SrSb_{кр.} + 46.6 \pm 2.3\ ккал.$$

$$3Sr_{кр.} + 2Sb_{кр.} = Sr_3Sb_{2\ кр.} + 136.3 \pm 1.2\ ккал.$$

$$2Sr_{кр.} + Sb_{кр.} = Sr_2Sb_{кр.} + 78.0 \pm 1.1\ ккал.$$

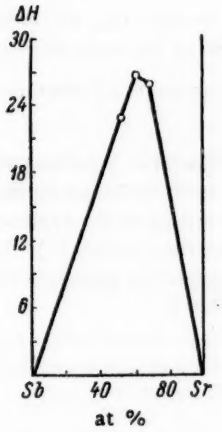

Fig. 3. The relationship between the enthalpies of formation of SrSb, Sr_3Sb_2 and Sr_2Sb, relative to one average gram-atom, and the composition.

Fig. 3 shows the relationship between the enthalpies of formation of SrSb, Sr_3Sb_2 and Sr_2Sb, relative to one average gram-atom, and the composition. The curve in Fig. 3 confirms the existence of the compounds Sr_3Sb_2 and Sr_2Sb. It is appropriate to mention that strontium forms a compound of formula Sr_2E with nitrogen [4], antimony and bismuth [1]. The formation of a compound with this composition of elementary substances does in fact correspond to the greatest contraction in the Sr–Sb system (Fig. 1).

SUMMARY

1. The existence of the compounds $SrSb_3$, SrSb, Sr_3Sb_2 and Sr_2Sb has been established in the Sr–Sb system.

2. The enthalpies of formation found for SrSb, Sr_3Sb_2 and Sr_2Sb are equal to −46.6 ± 2.3, −136.3 ± 1.2, −78.0 ± 1.1 kcal per gram-formula respectively at 25°.

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THE MAGNETIC SUSCEPTIBILITY OF STRONTIUM SUBNITRIDE

S. M. Ariya, M. S. Erofeeva and G. P. Mochalov

Discussion has been going on for a considerable time in the literature on the question of whether the substances with empirical formula CaCl, BaBr etc. are mixtures of the alkaline earth metal and its normal halide, or individual chemical compounds – subhalides. Cubicciotti and Thurmond [1] found that even in the fused state the alkaline earth metal and its halide form a heterogeneous system, and only an extremely limited mutual solubility is observed. Ehrlich [2] and Wenner [3] have prepared and described calcium subchloride CaCl; in addition Ehrlich reports the results of an x-ray crystallographic study of this compound. We have tried to reproduce the experiments of Ehrlich and Wenner, but in every case, no matter how we varied the experimental conditions, the material with empirical formula CaCl proved to be a mixture of CaCl and metallic calcium. Ehrlich [4] himself has recently admitted his error and has pointed out that the substance to which he ascribed the composition CaCl was in fact calcium hydrochloride CaHCl. Evidently the only compounds in which the alkaline earth metals are formally monovalent (in part) are the subnitrides of strontium and barium Sr_2N and Ba_2N prepared by S. M. Ariya, E. A. Prokofieva and I. I. Matveeva [5]. It is appropriate to mention at this point that compounds of the type Sr_2E have been detected in the Sr–Bi and Sr–Sb systems, i.e., this compound type is apparently characteristic of the systems formed by strontium and an element of the main subgroup of Group V.

Since the nitrogen in the subnitrides is evidently trivalent, one of the two atoms of strontium or barium in their subnitrides must be formally monovalent.

In order to find the true valence state of the strontium in Sr_2N we undertook the determination of its magnetic susceptibility. The measurements of the magnetic susceptibility were made by Gouy's method using a quartz torsion microbalance with electrodynamic compensation of the forces arising on the application of the magnetic field to the specimen. The strontium subnitride was prepared as described earlier [5]. The results of the measurements of the magnetic susceptibility of the strontium subnitride and of the strontium nitride which was decomposed in vacuo to prepare the subnitride specimen are given in Table 1.

TABLE 1

The Relationship Between the Magnetic Susceptibility of Strontium Nitride and Strontium Subnitride and Temperature

Temperature	Magnetic susceptibility (per gram-formula · 10^6)	
	Sr_3N_2	Sr_2N
20°	279	155
100	250.3	145
200	250.3	119

If one of the two strontium atoms in strontium subnitride Sr_2N were using only one of its two valence electrons for chemical bonds, its magnetic susceptibility at a temperature of 20° should amount to $1270 \cdot 10^{-6}$ per gram-formula. The value found experimentally is considerably (11 times) less. At the same time the strontium nitride Sr_3N_2 which served as starting material for the preparation of the subnitride is also paramagnetic. The nitride of normal composition Sr_3N_2 should be diamagnetic. The paramagnetism which we observed was explained by the presence of iron in the specimen being studied. Consequently, the value found by us for the magnetic susceptibility of strontium subnitride is very high, i.e., pure strontium subnitride is either weakly paramagnetic or completely diamagnetic. In other words, there is no monovalent strontium in strontium subnitride Sr_2N. All the strontium atoms use both of their valence electrons in the formation of chemical bonds.

Since the nitrogen atom in strontium subnitride, as in other nitrogen compounds of metals, probably uses three electrons for the formation of chemical bonds, it may be taken that three electrons out of the four valence electrons from two strontium atoms are used in bonds with the nitrogen atoms, while the fourth forms a bond similar to a metallic bond. This agrees with the previously established fact [5] that in the analogous Ba–N system the change from the nitride Ba_3N_2 to the subnitride Ba_2N is marked by a sharp increase (of several orders of magnitude) in the electrical conductivity. The temperature coefficient of electrical conductivity of barium subnitride is negative, which likewise confirms the metallic nature of the substance.

Compounds with metallic-like bonds are very common among the compounds of the elements of the supplementary groups, but are not characteristic of the elements of the main subgroups. From this point of view it is of interest to note that even such active metals as strontium and barium are able to form compounds with metallic-like bonds with one of the typical nonmetallic elements.

The possibility of synthesizing barium subnitride Ba_2N and barium pernitride BaN_2 [6] under conditions of thermodynamic equilibrium with their decomposition products has been suggested on the basis of an application of the isoatom method put forward by S. A. Shchukarev [7]. The method is based on the fact that the ratio of the enthalpy of formation of compounds in a system of two elements to the number of atoms of both elements in the formulae of these compounds, i.e., the enthalpy of formation relative to one averaged gram-atom, changes regularly with the composition of the compounds. This makes it possible to estimate, often with sufficient accuracy for practical purposes, the unknown values of the enthalpies of formation.

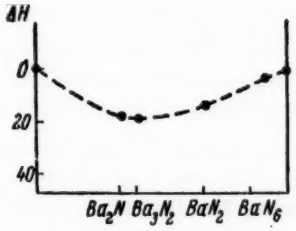

Fig. 1. The isoatom of the enthalpies of formation in the Ba–N system.

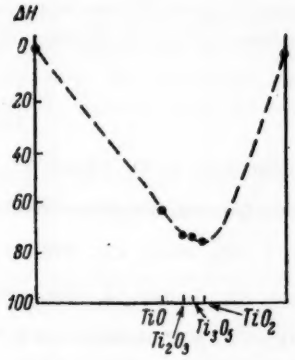

Fig. 2. The isoatom of the enthalpies of formation in the Ti–O system.

The isoatom of the enthalpies of formation in the Ba–N system are shown in Fig. 1 [8]. It can be clearly seen that the isoatom is characterized by one minimum corresponding to the composition of the nitride with the normal formula Ba_3N_2. There are ascending branches on both sides of this composition. In the nitride Ba_3N_2, all the valence bonds of the barium atom are saturated by nitrogen. At this composition, therefore, there are only Ba–N bonds, i.e., bonds between atoms of different elements. As we change to Ba_2N, part of the Ba–N bonds are replaced by Ba–Ba bonds. As we move toward the side corresponding to a higher nitrogen content (toward BaN_2–BaN_6), on the other hand, part of the N–Ba bonds are replaced by N–N bonds. In other words, as the composition changes in both directions away from that of the compound with the normal formula toward the sub- and per-compounds, a definite fraction of the bonds between atoms of different elements are replaced by bonds between atoms of the same element. As is well known, the stability of a bond between two atoms of different type is, in the majority of cases, greater than the arithmetic mean of the stabilities of the bonds formed by the corresponding atoms among themselves. This explains the fact that the minimum of the enthalpy of formation relative to one averaged gram-atom corresponds to the compound with normal composition, while the change to sub- or per-compounds is characterized by a regular increase in the corresponding branches of the isoatom.

The data on the chemical structure of strontium subnitride obtained on the basis of the measurement of the magnetic susceptibility of the compounds Sr_3N_2 and Sr_2N (the presence in these compounds of a metallic type of bond between the strontium atoms) confirms this interpretation of the shape of the isoatom put forward by S. A. Shchukarev.

From the point of view of the interpretation of the shape of the isoatom of the enthalpies of formation, the Ba–N system is one of the simplest – in this case the fact that compounds with bonds between identical atoms appear in the appropriate composition regions is quite clear. In other cases the true valence states of the elements as the composition of the compounds changes may be different, and accordingly the reasons for the regular shape of the isoatom may also be somewhat different, but systems of the Ba–N type are probably more common than might appear at first glance. Thus, for example, in the Ti–O system the oxides TiO and Ti_2O_3 should be strongly paramagnetic substances if the titanium atoms in these compounds were di- and trivalent. In fact these compounds are very weakly paramagnetic. In all the compounds in the Ti–O system the titanium atoms probably use all four of their valence electrons for the formation of bonds, i.e., in spite of the change in the composition of the compounds, the true valence state of the titanium atoms remains in fact constant. In other words, in the Ti–O system the regular shape of the isoatom (Fig. 2) [9] may also be interpreted as the result of the change in the proportions of bonds between atoms of different type and bonds between identical atoms.

SUMMARY

1. It has been established on the basis of data on the magnetic susceptibility of strontium subnitride that this compound contains no monovalent strontium. One of the four valence electrons from two strontium atoms is not used in a bond with nitrogen but forms a metallic type of bond in the lattice.

2. A discussion is given of some of the reasons for the presence of one minimum on the isoatom of the enthalpies of formation and for the regular change in these enthalpies in both directions away from the minimum.

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THE ENTHALPY OF FORMATION OF STRONTIUM ARSENIDE Sr_3As_2

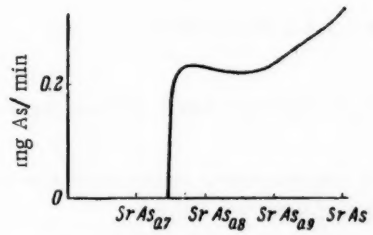
S. M. Ariya, Kan Kho-in, Yu. Barabanel and G. M. Loginov

The Sr–As system, as far as we are aware, has not been studied, and for this reason the present work was begun with a check on the actual existence of the compound Sr_3As_2. With this aim a series of experiments was arranged to study the vapor pressure of arsenic over specimens of strontium arsenides of different composition (Knudsen's effusion method).

The specimens were prepared by the action of arsenic vapor on metallic strontium obtained by a high-vacuum aluminothermic process. The calculated quantities of strontium and arsenic were placed in two small boats in a glass tube, which was then thoroughly evacuated and sealed. The tube containing the strontium and arsenic was then placed in a furnace whose temperature was slowly raised to 400°. During prolonged heating at this temperature the arsenic was quantitatively absorbed by the strontium. In order to make the specimens homogeneous, the boat containing the strontium arsenide was then placed in a quartz ampoule which was evacuated and sealed. The specimen was ignited over a prolonged period in this ampoule with the temperature gradually rising to 900°. Since quartz glass is not completely impervious to gases at this temperature, the ampoule was placed in a quartz tube in which continuous exhaustion using a mercury diffusion pump was employed to maintain a high vacuum throughout the heating process.

The apparatus used for the determination of the vapor pressure of As over the strontium arsenide specimens consisted of a vertical quartz tube placed in a furnace and connected to a high-vacuum apparatus, maintaining a vacuum of $(1 \text{ to } 3) \cdot 10^{-5}$ mm in the tube at 900°.

When the tube had attained a constant temperature (900°) and had been maintained under high vacuum for a prolonged period, the quartz ampoule containing the specimen was lowered into it using an electromagnetic device. The quartz ampoule was closed with a thin quartz sheet pierced with a round opening made using the narrow flame from a small oxygen–gas burner. The temperature of the furnace during the experiments was maintained constant to within 1-2°.



The relationship between the reduction in weight of an ampoule containing strontium arsenide after being heated for 1 minute, and the composition of the arsenide (abscissae – number of arsenic atoms per strontium atom).

The determination of the absolute values of the arsenic vapor pressure by Knudsen's method is not possible in the present instance, since the molecular composition of the arsenic in the vapor is not known exactly, i.e., the proportion of As_2 and As_4 molecules is not known. This was not essential for our purposes, however, since it was only necessary for us to establish whether a sudden change took place in the dissociation pressure at the composition Sr_3As_2, and this could be brought about only by a change in the phase composition of the arsenide at that composition, since the equilibrium $As_4 \rightleftharpoons 2As_2$ is homogeneous and, although able to change as the total pressure of arsenic in the vapor changes, will do so smoothly, without sudden changes. We therefore did not calculate the absolute magnitudes of the arsenic vapor pressures but used the values of the reduction (within a definite time interval) of the weight of the specimen, which takes place as a result of

the volatilization of arsenic through an opening of constant diameter at constant pressure. This value, in the light of the requirements of the present work, may be taken as the proportional vapor pressure.

The vapor pressure of arsenic over a specimen of the composition Sr_3As_2 at 900° is imperceptibly small. Over a specimen of the composition SrAs the vapor pressure of arsenic is measureable, but is much less than that of free arsenic at this temperature, which indicates that the specimen with this composition is not a mixture of strontium arsenide Sr_3As_2 and free arsenic, but contains some higher arsenides of strontium. The sudden fall in the curve of "arsenic vapor pressure against composition of the solid phase" (Fig.) shows clearly the existence of the compound Sr_3As_2.

The enthalpy of formation of strontium arsenide Sr_3As_2 was determined from the value of the enthalpy of its reaction with dilute hydrochloric acid and the value of the enthalpy of the reaction with hydrochloric acid and bromine.

The reaction of strontium arsenide with dilute hydrochloric acid takes place according to the equation

$$Sr_3As_{2s} + 6HCl_{aq} = 3SrCl_{2}aq + 2AsH_{3g}$$

As well as arsine AsH_3, however, there is also formed small amounts of a solid arsenic hydride.

The values found calorimetrically for the enthalpy of this reaction (the calorimetric method for the determination has been described earlier [1]) were −211.91, −210.82, −211.97, −210.14 from which the mean value is −211.1 ± 1 kcal per gram-formula Sr_3As_2.

From the known values of the enthalpies of formation and solution of hydrogen chloride and strontium chloride [2] and the recently determined enthalpy of formation of arsine [3] (18.0 ± 1.5 kcal / mole), the value obtained for the enthalpy of formation of strontium arsenide was −144.1 ± 2 kcal.

In addition, we determined the enthalpy of the reaction between strontium arsenide and dilute hydrochloric acid saturated with bromine and containing an excess of the latter (1), and the enthalpy of the reaction of free arsenic with the same solution (2). These determinations gave the following results: for reaction (1) the enthalpy change was −535.7 kcal / gram-formula Sr_3As_2, and for reaction (2) −59.0 kcal / gram-atom arsenic. We do not know whether all the arsenic in solution at the end of these experiments is in the pentavalent state, but this is not essential; the most important fact is that it is possible to assume, with a high degree of probability, that the ratio of the quantities of arsenic in different valence states is the same in both cases. This makes it possible to use the following thermodynamic cycle:

$$Sr_3As_s = 3Sr_s + 2As_s - Q_{Sr_3As_2},$$

$$2As_s + Br_l + HCl_{aq} = \ldots + 2Q_1,$$

$$3Sr_s + 3Br_l = 3SrBr_{2s} + 3Q_2,$$

$$3SrBr_{2s} + nH_2O = 3SrBr_{2aq} + 3Q_3,$$

$$-Q_{Sr_3As_2} + 2Q_1 + 3Q_2 + 3Q_3 = -Q_{Sr_3As_2} + 118 + 513 + 48.2 = 535.7.$$

The enthalpy of formation of strontium arsenide is thus found to be equal to −143.5 ± 2 kcal / gram-formula.

The agreement between the results obtained using two different thermodynamic cycles enables us to assume the value −144 ± 2 kcal / gram-formula for the enthalpy of formation of strontium arsenide.

SUMMARY

1. It has been established that the compound Sr_3As_2 exists in the strontium–arsenic system, while the existence of higher arsenides is also possible.

2. The value found for the enthalpy of formation of strontium arsenide is equal to −144 ± 2 kcal / gram-formula.

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THE ENTHALPIES OF FORMATION OF POTASSIUM ANTIMONIDE AND POTASSIUM BISMUTHIDE

M. P. Morozova, L. Getskina and M. Golomolzina

Values for the enthalpies of formation of potassium antimonide and potassium bismuthide K_3Sb and K_3Bi have been calculated by O. Kubashevsky and E. Evans [1] on the basis of an indirect determination of the heats of reaction of the components leading to the formation of these compounds. According to the data given by these authors, the enthalpy of formation of K_3Sb is -45.0 ± 8.0 while the enthalpy of formation of K_3Bi is -50.0 ± 9.0 kcal / gram-formula.

It did not seem probable to us that the heat of formation of the bismuthide should be greater than the heat of formation of the antimonide, since this does not agree with the usual order of the heats of formation of compounds of antimony and bismuth with metals. Indeed, the heat of formation of magnesium antimonide Mg_3Sb_2 is 80 ± 1 kcal / gram-formula and is thus twice as high as the heat of formation of magnesium bismuthide (40 ± 1 kcal / gram-formula [2]); the heat of formation of zinc antimonide is fairly high (48.0 ± 1.3 kcal / gram-formula [3]), whereas Zn_3Bi_2 has not been prepared at all, etc. We made an attempt to check the values for the enthalpies of formation of K_3Sb and K_3Bi.

The potassium antimonide and bismuthide specimens were prepared by fusing the metals together in stoichiometric amounts in hermetically sealed steel crucibles (K_3Sb at 850°, K_3Bi at 700°). The K_3Sb alloy had a greenish-violet color and was readily hydrolyzed in air; the K_3Bi had a yellow color and was also hydrolyzed in air. Analysis of the specimens obtained showed that fusion had brought about no perceptible change in the compositions taken for the reaction.

In order to determine the enthalpies of formation we used the reactions of these compounds with dilute hydrochloric acid (0.9 N), which proceeds quantitatively according to the equations

$$K_3Sb_s + 3HCl_{aq} = 3KCl_{aq} + Sb_s + 1.5H_2g \quad (1)$$

$$K_3Bi_s + 3HCl_{aq} = 3KCl_{aq} + Bi_s + 1.5H_2g \quad (2)$$

In order to avoid the possibility of formation of significant amounts of stibine in the reaction of K_3Sb with acid, reaction (1) was carried out in the calorimeter using a solution of hydrochloric acid in which a certain amount of potassium antimonide had previously been dissolved and which, as a result, contained highly dispersed metallic antimony in the form of a suspension which catalyzes the decomposition of stibine.

Reaction	Heat of reaction (in kcal / gram-formula)			
	Alloy No.	mean value	Alloy No	mean value
(1) $K_3Sb_s + 3HCl_{aq} = \ldots$	111.1	108.0	111.0	110.0
(2) $K_3Bi_s + 3HCl_{aq} = \ldots$	126.8	127.0	128.3	127.3

The method used in the calorimetric determinations has been described by us earlier [4].

The data obtained by us for the heats of reactions (1) and (2) are given in the Table.

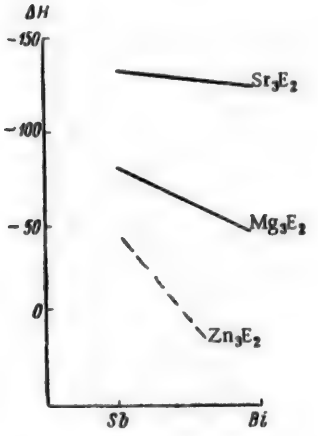

Fig. 1. The heats of formation of the antimonides and bismuthides of magnesium, strontium and zinc.

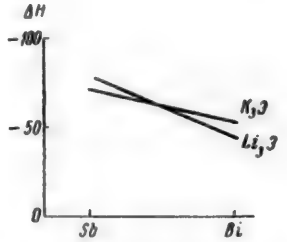

Fig. 2. Enthalpies of formation of potassium and lithium antimonides and bismuthides.

Using the known values for the enthalpies of formation and solution of HCl and KCl [5], we obtain, for the enthalpies of formation of K_3Sb and K_3Bi,

$$3K_s + Sb_s = K_3Sb_s + 71.4 \pm 2 \text{ kcal}$$
$$3K_s + Bi_s = K_3Bi_s + 54.1 \pm 1 \text{ kcal}$$

The change from potassium antimonide to potassium bismuthide is thus accompanied by a reduction in the heat of formation analogous to that observed in the case of the compounds of antimony and bismuth with other metals. It is a striking fact that in the case of the compounds of antimony and bismuth with divalent metals the reduction in the heats of formation as we go from the antimonide to the bismuthide is more sharply shown, the higher the ionization energy of the metal atoms (Fig. 1).

As far as the compounds of antimony and bismuth with the alkali metals are concerned, thermodynamic data are only available for the lithium and potassium compounds; in this case also (Fig. 2) the increase in the ionization potential from potassium to lithium corresponds to a sharper decrease in the heat of formation as we go from the antimonide to the bismuthide.

SUMMARY

1. The enthalpy of formation of potassium antimonide K_3Sb has been found to be equal to -71.4 ± 2 kcal / gram-formula.

2. The enthalpy of formation of potassium bismuthide K_3Bi has been found to be equal to -54.1 ± 1 kcal / gram-formula.

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THE MECHANISM OF METAL ELECTRODEPOSITION FROM SOLUTIONS OF SIMPLE AND COMPLEX SALTS

A. I. Levin

At the present time there is sufficient literature and experimental data to show that in an electrode process the ions taking part are not free simple ions, but are always complex or hydrated ions, irrespective of the sign of their charge [1]. Experimental proofs of the accuracy of this hypothesis were earlier obtained in work by O. A. Essin [2] and A. I. Levin [3], in which several branches were detected on the polarization curves in the case of the precipitation of metals from their simple and complex electrolytes. In this work the existence of two, three and more breaks in the curve was explained by the discharge of the different ions present in the solution being studied.

In the analysis, in each case, of the problem of which ions are taking part in the cathode reaction, it has to be borne in mind that, in the absence of any current flowing in the solution, and with a given cation (for example, copper) present together with an excess of a complex-forming substance (for example, potassium cyanide) a whole series of complex forms may exist, for example, $Cu(H_2O)^{\cdot}$, $CuCN$, $Cu(CN)_2^{'}$, $Cu(CN)_3^{''}$, $Cu(CN)_4^{'''}$ etc., whose concentration is determined by their instability constants and by solvation equilibria.

In contrast to ionic and acid-base equilibria, which are established practically instantaneously, solvation equilibria of the type $[M(Q)_x] + nH_2O \rightarrow M(H_2O)_p^{\cdot} + xQ(H_2O)_q^{'}$ proceed over a time interval. The rates of the reactions of complex formation may differ by multiples of the order of 10^{10}, which corresponds to a difference in activation energies of 14 kcal [4]. At the same time, polyvalent ions, in reactions with other ions in the solution and with molecules of solvent, may split up to give simpler compounds [5]. Consequently, although the concentration of one of the ions may exceed that of the others, the existence of its homologs in the electrolyte is by no means excluded [6].

It is difficult to tell beforehand, in a particular case, which of the ions present in a solution are taking part directly in the electrode reaction. Gerischer [7], on the basis of direct measurements of the exchange current density i_0 of zinc and cadmium electrodes in equilibrium, came to the conclusion that in the majority of cases the ions taking part in the discharge were complexes of the type $Zn(OH)_2$, $Zn(C_2H_4)$, $Zn(CN)_2$ etc., i.e., the compounds with low coordination number and smallest negative charge. The same conclusion was reached by A.G. Stromberg [8], who determined the composition of the zinc ions being discharged, from the difference in the anode and cathode half-wave potentials in the irreversible electrode process at a dropping amalgam electrode.

It has been shown earlier in our work [9] that in those cases where two complex-forming species are present in solution, the less stable complex takes part in the discharge process. Thus, for example, when sodium citrate is added to a copper pyrophosphate electrolyte, $Cu(C_6H_5O_7)^{'}$ ions are reduced at the cathode, while the concentration of $Cu(P_2O_7)_2^{-6}$ or $Cu(P_2O_7)^{-2}$ remains high.

It should be noted that since the overwhelming majority of solutions of complex compounds belong to the class of strong electrolytes and obey the same laws as simple strong electrolytes, the equilibrium state of such systems cannot indicate the composition of the ions predominating in the solution layers next to the electrodes or the rate of their reaction in electrolysis. The exceptionally large changes in the nature and the shifts of the ionic equilibrium which are observed during electrolysis provide evidence for the fact that the thermodynamic stability of the complex does not predetermine the kinetics of the actual electrode process at a given current density. In actual fact the ions taking part in an electrode reaction may be not only the ions predominating in the electrolyte before the current is passed, but other ionic species which are formed and concentrated in the layers

close to the electrodes during the electrolysis process. The bath used for galvanic chromium plating may be taken as an example of this.

It is known that when no current is passing we have the equilibrium

$$2CrO_4'' + 2H^+ \rightleftarrows 2HCrO_4' \rightleftarrows Cr_2O_7'' + H_2O,$$

which is moved to the left as the pH is increased and the solution is diluted. The studies which we have made of the concentration changes in the layers close to the electrodes in chrome baths, together with measurements of electrode polarization [10] show that extensive shifts in the ionic equilibrium in the catholyte take place as the current density is increased. On the first part of the $i - \varphi$ curve (Fig. 1), i.e., at relatively low current densities (pH 0.08–0.2), reduction of Cr_2O_7'' anions to trivalent chromium takes place, according to the reaction

$$Me\,(Cr_2O_7'')_{ads} + 6e + 14H^+ \longrightarrow Cr^{+++} + 7H_2O$$

(which agrees with the data given by A. T. Bagramyan and N. D. Usachev [11]). Increase of pH in the cathode zone to 2.6 with increase in current density leads to a shift of the ionic equilibrium in the direction of CrO_4'' formation, so that on the second part of the curve, together with the reduction of Cr_2O_7'' to Cr^{+++}, we have the process

$$Me\,(CrO_4'')_{ads} + 3e + 8H^+ \longrightarrow Cr^{+++} + 4H_2O.$$

Finally, on the third part of the $i - \varphi$ curve (at pH 3-4) the CrO_4'' completely displaces the previously absorbed Cr_2O_7'' ions from the cathode. These shifts in the ionic equilibrium with change in pH evidently take place instantaneously, as is confirmed, for example, by the study of the adsorption spectra [12]. As a result, the process of reduction of CrO_4'' ions to metallic chromium becomes possible

$$Me\,(CrO_4'')_{ads} + 6e + 4H_2O \longrightarrow Cr + 8OH$$

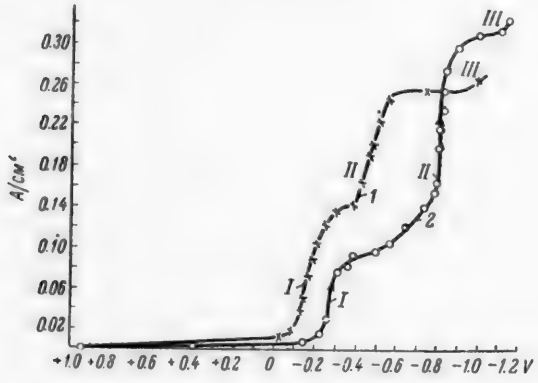

Fig. 1. Polarization of Pt cathode in solutions of chromic anhydride.
1) 1 M CrO_3 + 0.01 M H_2SO_4, 2) 2 M CrO_3 + 0.02 M H_2SO_4.

Discharge of H^+ ions and partial reduction of CrO_4'' to Cr^{+++} take place simultaneously. It is not difficult to see that at high current densities, as a result of chemical and concentration polarization and the accompanying discharge of hydrogen, the pH of the catholyte may move so far towards the alkaline region that the point of hydrate formation is reached (pH 5.3-6). The hydroxide and basic salts of chromium in the freshly-precipitated state have the properties of a gel, whose particles carry a positive charge. They are adsorbed by the surface of the cathode and in this way reduce its negative charge (the potential of zero charge for chromium lies at a approximately –0.45 v [13]). This last effect facilitates the discharge of chromate anions on the cathode.

Analogous phenomena are observed in a copper pyrophosphate bath. It may be taken as established that in this case the cathode process at relatively low $Na_4P_2O_7$ concentration and low current densities is the discharge of $Cu(P_2O_7)^{2-}$ anions (instability constant $K_1 = 1.2 \cdot 10^{-6}$). With increase in $Na_4P_2O_7$ content and current density, the equilibrium $Cu(P_2O_7)^{2-} \rightleftharpoons Cu(P_2O_7)_2^{6-}$ is moved in the direction of the hexavalent complex pyrophosphate anion, as a result of which the previously adsorbed $Cu(P_2O_7)^{2-}$ anions are displaced from the cathode surface by $Cu(P_2O_7)_2^{6-}$ ions (instability constant $K_2 = 1.3 \cdot 10^{-11}$ [14]). Outwardly these changes are shown in the constant value of the current over a fairly wide potential range (Fig. 2). After the limiting conditions for the discharge of the anions with the lowest negative charge have been reached, we have the second part of the $i - \varphi$ curve corresponding to the discharge of $Cu(P_2O_7)_2^{6-}$.

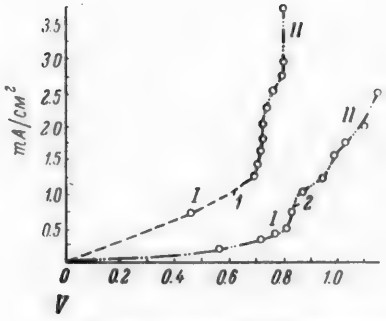

Fig. 2. Polarization of Cu cathode in pyrophosphate electrolytes.
1) 0.05 M $CuSO_4$ + 0.1 M $Na_4P_2O_7$
2) 0.06 M $CuSO_4$ + 0.153 M $Na_4P_2O_7$

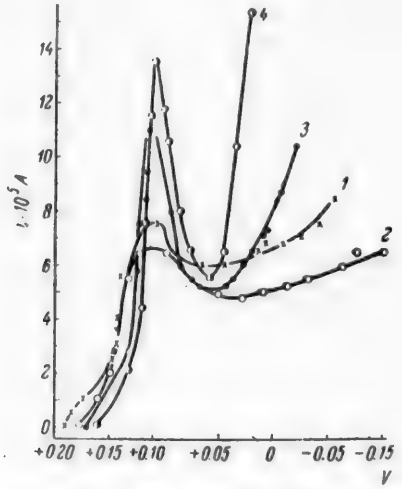

Fig. 3. Polarization of Cu cathode in pyrophosphate electrolytes near the zero charge point.
1) 0.0115 M $CuSO_4$ + 0.016 M $Na_4P_2O_7$
2) 0.0098 M $CuSO_4$ + 0.008 M $Na_4P_2O_7$
3) 0.02 M $CuSO_4$ + 0.03 M $Na_4P_2O_7$
4) 0.03 M $CuSO_4$ + 0.05 M $Na_4P_2O_7$

Experiment shows that no matter which of the anions indicated is reduced: $M[Cu(P_2O_7)^{2-}]_{ads.} + 2e \rightarrow Cu + P_2O_7^{4-}$, or $M[Cu(P_2O_7)_2^{6-}]_{ads.} + 2e \rightarrow Cu + 2P_2O_7^{4-}$, the result of the electrode reaction is the formation of a copper deposit on the cathode, accompanied simultaneously by an increase in the $P_2O_7^{4-}$ concentration in the catholyte [15]. This last effect results in the formation of very thin (apparently monomolecular) adsorbed layers consisting of compounds of the type $Cu^{\cdot\cdot} - P_2O_7^{\cdot\cdot\cdot\cdot} - Cu^{\cdot\cdot}$. When concentrated solutions of the pyrophosphate complex are used, the formation of salt films of crystalline structure as a separte phase is observed [16].

The formation of films of varying structure and composition, passivating the surface of the cathode, is also possible in a particular case as a result of changes in pH and shifts in the ionic equilibrium taking place in the region close to the electrode.

Further studies have shown that in a pyrophosphate complex electrolyte [17] and in a chrome bath [18], besides the formation of stable, compact adsorbed layers, we have the specific phenomenon of retardation of the cathode process of reduction of the complex anions. This effect is observed as the potential passes through the point of zero charge (Fig. 3). This is shown outwardly by the onset of sudden fall of current on the $i - \varphi$ curves. This drop in the current, in agreement with A. N. Frumkin's retarded discharge theory, may be explained by recharging of the surface and the development of repulsive forces between the cathode and the negatively charged complex ions [19].

As follows from Fig. 3, the zero charge point for copper in a pyrophosphate bath is close to + 0.05 v. Thus over a fairly wide working range of current density (Fig. 2) the cathode surface has a positive charge (the left-

hand ascending portion of the electrocapillary curve). In this case the adsorption of anions of the type $Cu(P_2O_7)^{2-}$, $Cu(P_2O_7)_2^{6-}$ etc. is facilitated.

When considering the ability of the complex anions to be discharged not only on the positively charged surface of the electrode, but also after the drop in current, when the cathode surface acquires a large negative charge (the right-hand branch of the electrocapillary curve), it should be noted that different authors explain this experimental fact in different ways. Billiter [20] suggests that in the cathode field the complex anions behave as dipoles, with their positive poles, i.e. the metal cation, turned toward the electrode. As a result of the "stretching" of the complex ion, from the electrostatic forces, the removal of the metal is facilitated. T. A. Kryukova [21] explains the ability of anions to be discharged on the cathode as due to the screening effect of stray positive ions present in the solution, while these positive ions, for some reason or other, , cannot be discharged themselves. Indeed, studies of the effect of small additions of tetrabutylammonium sulfate (0.03-0.3 mg/ liter) have shown [17, 18] that these additions lower the cathode polarization in the discharge of anions of the type $Cu(P_2O_7)_2^{6-}$. The $\varphi - f(c)$ curve is asymptotic; this fact provides evidence that the effect of the cationically active additions is due to their adsorption characteristics.

The adsorption of tetrabutylammonium cations makes the adsorption potential ψ_1 more positive; from this it follows that the polarization ($\Delta\varphi$) should decrease. In fact, it follows from A. N. Frumkin's equation for the retarded discharge

$$\Delta\varphi = a + \frac{n_a + \alpha}{\alpha}\psi_1 - \frac{RT}{\alpha n_k F}\ln i$$

that the surface concentration of the anions being reduced at the cathode depends on all the factors which influence the ψ_1 potential.

The value of the ψ_1 potential may be given approximately by the expression

$$\psi_1 = \text{const} + \frac{2RT}{n_a F}\ln(\pm\varphi_a) - \frac{RT}{n_a F}\ln c$$

Here: c is the electrolyte concentration, n_a is the valency of the complex anion, and φ_a is the potential at the electrode surface, relative to the potential in the bulk of the solution, taken arbitrarily as zero [22]. A plus sign is put before φ_a if $\psi_1 > 0$, a minus sign if $\psi_1 < 0$.

The value of ψ_1 thus depends on the total electrode potential, the electrolyte concentration, the valence of the ions, the presence of extraneous added reagents, etc. When the surface-active tetrabutylammonium cations are adsorbed, they reduce the negative charge on the cathode and thus facilitate the reduction of the complex pyrophosphate anions on the cathode. We have seen that in the case of a chrome electrolyte a similar part is played by the hydroxide and basic salts of chromium.

Thus when chrome and certain other complex electrolytes are used, the part of the extraneous capillary-active added reagents, which influence the kinetics of the electrode reactions, is played by substances formed directly in the layers near the electrode during the electrolysis process. The determining factor is here the screening of the negatively charged cathode surface, as a result of which the activation energy required for the reduction of the chromate anions to the metal is lowered.

Finally, A. N. Frumkin suggests [23] that the reaction involving the reduction of the anions on the negatively charged surfaces may take place via a tunnel mechanism, without direct contact between the ions being discharged and the metal of the electrode.

In this connection we would point to a number of works by foreign authors, who have shown with the help of labeled atoms that a rapid exchange reaction can take place between polyvalent anions such as $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. The analogy between these charge exchange reactions and the reduction of anions at the strongly negatively charged metal surface speaks for itself.

There are thus many facts in support of the hypothesis that complex anions take part directly in the cathode process.

The point of view put forward concerning the mechanism of electrocrystallization has proved extremely fruitful in connection with the improvement and control of electrode reactions in a copper pyrophosphate bath and in the galvanic chromium plating process.

SUMMARY

1. Studies carried out have provided evidence that there is no special mechanism for the discharge of ions from complex electrolytes in comparison with solutions of simple salts, since in all cases the ions taking part in the cathode process are not simple ions but complex or solvated ions.

2. The discharge potentials of ions are directly dependent on the stability of the appropriate complexes and on their charge: a) if the complex is not very stable and the excess of complex-forming species sufficiently small, the discharge of "simple", i.e., hydrated, metal cations becomes possible; b) if the stability of the complex is sufficiently high, and the concentration of the complex-forming species negligible, then it is more probable that the lower complex form will take part in the discharge; for example, when $Cu(P_2O_7)^{2-}$ and $Cu(P_2O_7)_2^{6-}$ are present the process $Cu(P_2O_7)^{2-} + 2\bar{e} \rightarrow Cu + P_2O_7^{4-}$; c) if the concentration of complex-forming species is high, then at sufficiently high current densities more complex anions may be reduced on the cathode, for example: $Cu(P_2O_7)^{6-} + 2\bar{e} \rightarrow Cu + P_2O_7^{4-}$ etc.

3. The concentration changes in the layers close to the electrodes, which take place during electrolysis, may lead to sudden shifts in the ionic equilibria and to the formation of new complex species.

4. In the mechanism of electrochemical electrode reactions, a special role is played by the position of the zero charge point characteristic of a given metal. A knowledge of the value of the zero charge potentials is necessary for the determination of the charge of the electrode surface, and hence for the determination of the conditions under which the electrode reaction should take place.

5. Adsorption processes at the metal–solution boundary have a very real influence on the course of the electrode reaction. In a number of cases they facilitate the reduction of the complex anions on the negatively charged cathode surface.

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ALKYLCARBONATES III. USE OF TAGGED ATOMS (OXYGEN ISOTOPE C^{14}) IN THE INVESTIGATION OF THE MECHANISM OF THERMAL DECOMPOSITION OF ALKYLCARBONATES.

V. I. Kurov

In a previous communication [1] it has been suggested that in the thermal decomposition of sodium alkylcarbonates the carbon monoxide that is evolved is formed from the carbon of the carbonate group, but only indirect evidence was adduced in explanation of this. By the use of the carbon isotope C^{14} (designated below by an asterisk) it has been possible to confirm that in the thermal decomposition of $C_2H_5OC^*OONa$ and CH_3OC^*OONa carbon monoxide actually is formed from the carbonate carbon.

Sodium ethylcarbonate, $C_2H_5OC^*OONa$, was prepared by the following means. 0.034 g of BaC^*O_3 with a total activity of 1 mCu and 0.2 g of freshly prepared $BaCO_3$ were mixed in a small Würtz flask and hydrochloric acid was added from a dropping funnel. The C^*O_2 produced was purified and dried, then drawn with a current of air by means of an aspirator through a cooled ethanol solution of sodium alcoholate. After the air had been drawn through the alcoholate for a half hour, then ordinary carbon dioxide gas was passed through for 2 hours. The sodium ethylcarbonate $C_2H_5OC^*OONa$ formed was filtered off and washed with ether, the remainder of which was removed by a current of dry air.

Found %: Na 20.39, 20.22. $C_3H_5O_3Na$. Calculated %: Na 20.52.

β-Ray analysis of 2 mg of the salt that was obtained showed 10^5 imp./min.

Thermal decomposition of the $C_2H_5OC^*OONa$ was carried out at 280-295°. 5.6 g of the salt was used. Analysis of the gas calculated on the 100% basis showed that it contained 46.7% CO_2, 14.3% C_2H_4, and 39.0% CO.

In order to verify the presence of C^{14} in the carbon monoxide it was converted to carbon dioxide. For this purpose the carbon monoxide was passed with a current of oxygen through red-hot copper oxide in an organic combustion tube. The carbon dioxide gas coming out of the tube was absorbed in a saturated solution of barium hydroxide. The barium carbonate obtained was filtered off, washed with water, then with ethanol, dried, and subjected to β-ray analysis, which was found to equal 800 imp./min for 1.5 mg.

The preparation of the ethylcarbonate $C_2H_5OC^*OONa$ described above and its thermal decomposition can be represented by the following basic equilibria

$$Ba\overset{*}{C}O_3 + 2HCl \longrightarrow \overset{*}{C}O_2 + BaCl_2 + H_2O$$

$$\overset{*}{C}O_2 + C_2H_5ONa \longrightarrow C_2H_5O\overset{*}{C}OONa$$

$$C_2H_5O\overset{*}{C}OONa \xrightarrow{295^\circ} NaH\overset{*}{C}O_3 + C_2H_4$$

$$C_2H_5O\overset{*}{C}OONa \xrightarrow{295^\circ} NaOH + \overset{*}{C}O + CH_3CHO$$

By passing C^*O mixed with oxygen through red-hot copper oxide and absorbing in barium hydroxide BaC^*O_3 is again formed.

$$2\overset{*}{C}O + O_2 \longrightarrow 2\overset{*}{C}O_2$$

$$\overset{*}{C}O_2 + Ba(OH)_2 \longrightarrow Ba\overset{*}{C}O_3 + H_2O$$

An experiment was also carried out with sodium methylcarbonate. The salt was prepared by drawing through a cooled methanol solution of sodium methylate for 20 minutes the C^*O_2 that was liberated by hydrochloric acid from 0.0587 g of BaC^*O_3 (total activity 3 mCu) and 0.15 g of $BaCO_3$. Then ordinary carbon dioxide gas was passed through for 1.5 hours.

Found %: Na 23.20, 23.31. $C_2H_3O_3Na$. Calculated %: Na 23.46.

For the thermal decomposition, which was carried out at 284-310°, 4.9 g of CH_3OC^*OONa was used. Analysis of the gas obtained, calculated on the 100% basis, showed that it contained 84.6% CO_2, 2.6% C_2H_4, and 12.8% CO. As in the preceding experiment, the carbon monoxide was burned in a current of oxygen: the carbon dioxide gas obtained was absorbed in barium hydroxide and the barium carbonate produced was subjected to β-ray analysis. The analysis gave a positive result.

SUMMARY

1. The method of tagged atoms has been used to investigate the mechanism of the thermal decomposition of alkylcarbonates.

2. The ethylcarbonate $C_2H_5OC^*OONa$ and the methylcarbonate CH_3OC^*OONa have been prepared, containing the isotope C^{14}.

3. By the use of the isotope C^{14} confirmation has been obtained of the suggestion made earlier that the carbon monoxide evolved upon thermal decomposition of alkylcarbonate salts is formed from the carbonate carbon.

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ELECTROLYTIC DISSOCIATION IN NONAQUEOUS SYSTEMS

V. THE SYSTEM PYRIDINE–ALLYL MUSTARD OIL

S. P. Miskidzhyan

In a series of our publications [1-4] it has been shown that in systems formed from allyl mustard oil and aromatic amines (aniline, piperidine) not only the substituted thioureas are produced, but also as byproducts the corresponding thiocyanoallylaniline and thiocyanoallylpiperidine, which are electrolytes.

In the present work we report the results of an investigation of the mechanism of the electrolytic dissociation of the compounds produced in the system pyridine–allyl mustard oil. This system has been studied only partially by physicochemical analytical methods. Thus, N. S. Kurnakov and S. F. Zhemchuzhny measured its viscosity and density at 25° and established that at this temperature there was no chemical reaction between the components of the system [5]. However, measurement of the specific electrical conductivity showed that its solutions were significantly conducting [6]. This circumstance, it appeared to us, was somewhat in disagreement with the results obtained by viscosity and density measurement. It is difficult to suppose that such a high conductivity developed in the system as a result of the dissociation of pyridine in mustard oil or of mustard oil in pyridine [7]. Obviously it must be assumed that even at such a low temperature (25°) a very weak chemical reaction occurs, as a result of which compounds are formed that are electrolytes. As will be shown below, our investigations have fully confirmed this proposition.

EXPERIMENTAL

Pyridine was dried over potassium hydroxide for a long time and redistilled. For our work the fraction boiling at 115-115.5° (740 mm), d_4^{20} 0.9825, n_d^{20} 1.5092 was collected. The allyl mustard oil was prepared by the method previously described [4]. The mixtures of the system were prepared by weighing. The solutions prepared

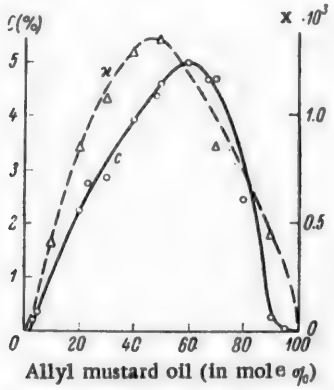


Fig. 1. Relation of allylpyridinium thiocyanate concentration (C) and specific conductivity (x) to the composition of mixtures of the system pyridin–allyl mustard oil.

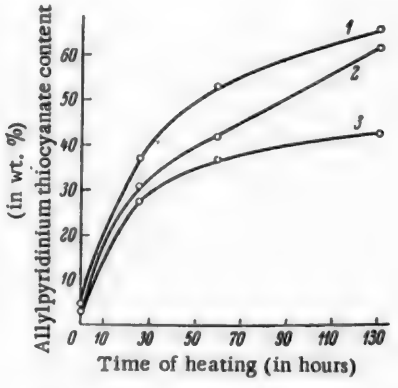


Fig. 2. Relation of allylpyridinium thiocyanate concentration to time of heating some mixtures of the system. Allyl mustard oil content of mixture (in mole %): 1) 50.9, 2) 60.8. 3) 30.6.

were stored in dark, ground glass-stoppered bottles, which were kept in a desiccator. Almost all the mixtures turned very brown when kept. In most of the solutions of this system we found the ion CNS^- by the methods that we used in our previous work on the investigation of systems formed from allyl mustard oil and amines. In Fig. 1 are presented the results of measurements of the CNS^- ion concentration (colormetric method) in relation to the composition of the mixture (time of storage of mixtures 2 months). The dashed curve shows the isotherm of the specific conductivity of the system with a storage period of 1 month (according to the data of N. K. Voskresenskaya). As can easily be seen, the CNS^- concentration in the system changes in accord with the specific conductivity. This provides a basis for assuming that the electrical conductivity of the system depends on the presence of CNS^- ions and some organic cation. Some mixtures of the system were subjected to prolonged heating at $100 \pm 5°$. In Figs. 2 and 3 the results of CNS^- ions measurements in relation to the period of heating are given.

The concentration of allylpyridinium thiocyanate in the individual mixtures reached 70 wt.% after heating, which is evidence of the great extent of this reaction. The extent of the reaction between the components of the system is also indicated by the viscosity and density data that we obtained after heating the mixtures of the system for 214 hours. These data are presented in the table.

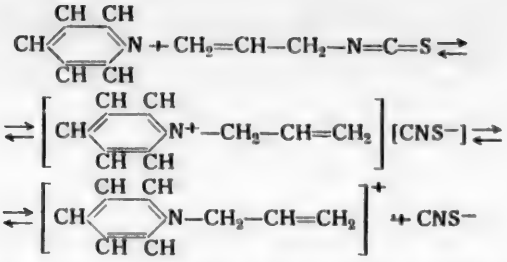
Viscosity, Density, and Electrical Conductivity of the System Pyridine–Allyl Mustard Oil in Relation to Period of Storage and Heating

Allyl mustard oil content (in mol. %)	d_4^{25}		η^{25} (in poises)		$x^{25} \cdot 10^3$	
	with 9-months storage period	After heating for 214 hours	with 9-months storage period	after heating for 214 hours	with 9-months storage period	after heating
5	0.9809	1.0153	0.00900	0.0110	—	3.875
10	0.9993	1.0420	0.01035	0.0142	1.809	5.153
20	1.0018	1.0671	0.01225	0.0214	1.920	5.154
30	1.0239	1.1483	0.01323	0.1034	2.540	4.428
33	1.0251	—	0.01449	—	—	2.173
40	1.0286	1.1853	0.01422	0.427	2.960	0.835
48	1.0294	1.2475	0.01372	10.43	—	—
50	1.0287	—	0.01390	—	3.500	0.434
52	1.0303	1.2573	0.01353	22.75	—	0.217
60	1.0309	1.2640	0.01328	47.80	3.940	0.128
70	1.0265	—	0.01273	—	2.960	0.167
80	1.0316	1.2166	0.01174	14.67	2.460	1.085
90	1.0245	1.1950	0.00990	1.54	1.780	

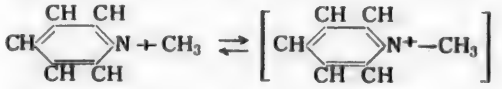
The presence of a sharply expressed maximum in the isotherms of internal friction and density is positive evidence of the formation of compounds between the components of systems. Upon long storage, as our data show, reaction takes place between the components of the system, and the longer the storage period, the greater the extent of the reaction. The reaction proceeds especially vigorously when the mixtures are heated.

We also measured the conductivity of solutions of the system in relation to storage period and time of heating. Comparison of the data of Fig. 1 and the table shows that the electrical conductivity increases greatly upon storage of the mixtures and is especially greatly increased when they are heated for a long time. This is in good agreement with the fact that the CNS^- concentration also greatly increases with the period of storage and particularly with the time of heating the solutions of the system. The minimum in the isotherm of the specific conductivity is explained by the high viscosity of the mixtures and, as is well known [8], indicates a reaction between the components of the system.

On the basis of all the above-mentioned experimental data we assume that upon storage of the solutions and also upon prolonged heating of them a chemical reaction takes place between pyridine and allyl mustard oil with the formation of allylpyridinium thiocyanate, which dissociates into thiocyanate ion and the corresponding organic cation according to the following scheme



This reaction is similar to the reaction well known in the literature between methyl iodide and pyridine according to the equilibrium



We succeeded in isolating the allylpyridinium thiocyanate formed in this way from the mixtures which were subjected to prolonged heating. For this purpose we made use of the good solubility of allylpyridinium thiocyanate in water. We extracted with water from the thermally treated mixtures the compound that was of interest to us, after which a dark colored, tarry material remained on the bottom. From the aqueous solution of allylpyridinium thiocyanate the water was distilled off on a water bath under a vacuum of about 10-20 mm. Colorimetric measurements of the CNS^- concentration showed that the dark brown, transparent, viscous liquid with d_4^{20} 1.2019 and n_D^{20} 1.6225 that we obtained in this way contained 98-100% of allylpyridinium thiocyanate.

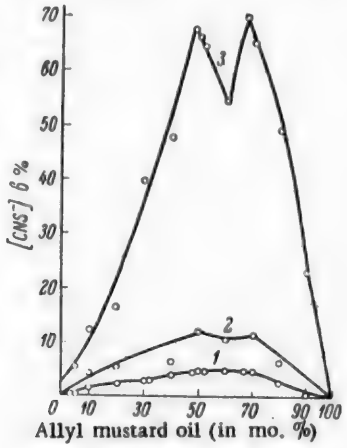


Fig. 3. Relation of CNS^- concentration (allylpyridinium thiocyanate) in the solutions of the system pyridine – allyl mustrard oil to the period of storage and time of heating. 1) storage period 2 months, 2) storage period 9 months, 3) after heating to 100° for 214 hours.

SUMMARY

The reaction between allyl mustard oil and pyridine has been investigated. It has been established that upon storage and especially upon prolonged heating, as a result of chemical reaction between the components of the system allylpyridinium thiocyanate is formed, the dissociation of which explains the high electrical conductivity of the system.

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TRANSFORMATIONS OF HYDROCARBONS IN THE PRESENCE OF OXIDE CATALYSTS

VIII. TRANSFORMATION OF n-HEXADECANE OVER A MOLYBDIC CATALYST

Yu. N. Usov and N. G. Mettsel

The transformations of n-alkanes with more than nine carbon atoms in the molecule over oxide dehydrocyclizing catalysts have been studied comparatively little. In this connection only the work of Rozenberg [1] deserves attention, in which he studied the character of the transformation of n-decane over an alumo-chromium catalyst and explained the reaction mechanism of its dehydrocyclization to aromatic hydrocarbons.

In the present work we have studied the transformations of n-hexadecane over a commercial molybdenum catalyst used for the aromatization of petroleum fractions.

TABLE 1

Conditions and Results of Experiments on the Transformation of n-Hexadecane Over a Molybdenum Catalyst (temperature 530°, volumetric rate of passage 0.5, duration of experiment 40 minutes)

Experiment No.	Experiment balance (in wt. %)			Specific gravity of liquid products d_4^{20}	Composition of gaseous products (in vol. %)			Yield of gas from 1 ml of raw material (in ml) (NTP)
	liquid products	gas	coke, tar, loss		H_2	C_nH_{2n+2}	C_nH_{2n}	
1	56.1	18.0	25.9	0.8719	93.0	5.5	1.5	540
2	61.3	17.4	21.3	0.8664	91.8	6.1	2.1	500
3	61.0	17.4	21.6	0.8680	—	—	—	510
4	63.2	17.4	19.4	0.8660	—	—	—	505
5	63.1	17.5	19.4	0.8658	—	—	—	500
6	63.7	16.9	19.4	0.8658	92.7	5.5	1.8	500

The conditions and the results for the experiments on the transformation of n-hexadecane over the molybdenum catalyst are presented in Table 1. In Tables 2 and 3 are presented data on the fractional distillation of the combined catalyzates from experiments 1-6 and the composition of the fractions obtained. From the data of Table 1 it is apparent that, notwithstanding the formation of coke and tar on the catalyst, its activity did not decrease during the series of experiments and the yield of liquid and gaseous products of the conversion of n-hexadecane was practically unchanged.

From an examination of the data presented it must be concluded that the extent of the conversion of n-hexadecane into aromatic hydrocarbons is very considerable under the conditions chosen. The results of fractional distillation of the catalyzate and the subsequent analyses of the fractions obtained indicate that the conversion of n-hexadecane over a molybdenum catalyst produces predominantly aromatic hydrocarbons boiling above 200°. The content of the latter in the catalyzate amounts to about 29 wt. %. The simplest aromatic hydrocarbons, which boil up to 200°, are present in the catalyzate in a smaller amount (18 wt. %).

The high-boiling aromatic hydrocarbons produced by the conversion of n-hexadecane are the result of a direct dehydrocyclization reaction. By oxidation of the catalyzate fractions and subsequent identification of the

products obtained it has been established that as a result of the dehydrocyclization of n-hexadecane principally o-alkyl-substituted homologs of benzene are formed, i.e., secondary carbon atoms of the starting alkane predominantly participate in the closing of the aromatic ring.

TABLE 2

Results of Fractional Distillation of Catalyzate from Experiments 1-6 (46.0 g used)

Boiling point of fraction	Yield		n_D^{20}	d_4^{20}	Bromine number	Aromatic hydrocarbon content (wt. %)
	(in g)	(in %)				
Up to 75°	0.30	0.65	—	—	—	—
75— 85	0.52	1.13	1.4358	—	25.0	29
85—105	0.69	1.50	1.4590	—	36.3	60
105—115	0.75	1.63	1.4604	—	30.1	64
115—130	0.77	1.67	1.4616	—	29.2	69
130—150	1.94	4.22	1.4733	0.8341	24.1	71
150—160	2.09	4.54	1.4810	0.8426	20.0	77
160—170	2.40	5.22	1.4877	0.8535	22.1	80
170—200	3.01	6.50	1.4690	0.8303	13.4	60
200—225	5.00	10.90	1.4738	0.8337	11.3	40
225—250	4.01	8.70	1.4727	0.8298	9.6	38
250—290*	21.29	46.30	1.4749	0.8332	9.5	45
Residue	2.03	4.35	—	—	—	—
Loss	1.20	2.60	—	—	—	—

TABLE 3

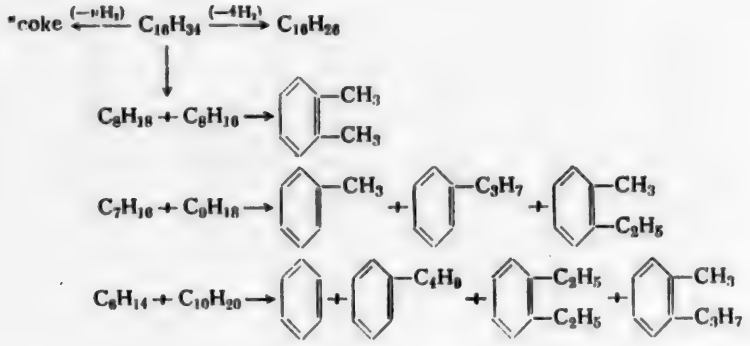
Identification of Aromatic Hydrocarbons in Fractions of Catalyzate.

Boiling point of fraction	Method of determination	Characterized through derivatives	Aromatic hydrocarbon contained in fraction
75-85°	Formolite test Nitration	Positive test Metadinitrobenzene, m.p. 89°	Benzene
85-115	Nitration	2, 4-Dinitrotoluene, m.p. 70.5°	Toluene
115-150	Oxidation	o-Phthalic acid, Phthalimide, m.p. 233°. Positive fluorescein reaction	o-Xylene
150-160	Oxidation	Benzoic acid, m.p. 121°	Propylbenzene
160-170	Oxidation	o-Phthalic acid, Phthalimide, m.p. 232.5-233°. Positive fluorescein reaction	o-Ethyltoluene
170-200	Oxidation	Benzoic acid, m.p. 121-121.5° o-Phthalic acid. Phthalimide, m.p. 232-233°. Positive fluorescein reation	Butylbenzene. o-Diethylbenzene. o-Propyltoluene.

The considerable hydrogen content of the gas (92%) and the large yield of gas (500 ml per 1 ml of raw material at NTP) indicate that destruction of n-hexadecane takes place also, along with the direct dehydrocyclization; thereupon the decomposition products formed are in their turn converted by dehydrocyclization into aromatic hydrocarbons boiling up to 200°. The breaking up of n-hexadecane takes place, apparently, chiefly at the middle or about the middle of the hydrocarbon chain. The unsaturated hydrocarbons formed as a result of cracking of n-hexadecane and its dehydrocyclization are present in all the fractions of the catalyzate.

Identification of the aromatic hydrocarbons in the catalyzate fractions that boil up to 200° has established the presence in them of benzene, toluene, o-xylene, propylbenzene, o-ethyltoluene, butylbenzene, o-ethylbenzene, and o-propyltoluene.

On the basis of the data obtained it is possible to propose the following scheme for the conversion of n-hexadecane over a molybdenum catalyst.



As is well known [2], the dehydrocyclization of alkanes and alkenes with 6 and 7 carbon atoms in the chain proceeds less rapidly than dehydrocyclization of aliphatic hydrocarbons with 8 and more carbon atoms in the chain. In particular therefore, the content of benzene and toluene in the catalyzate does not correspond to the amount of aromatic hydrocarbons with C_3- and C_4- substituents in the benzene nucleus, although in the primary breakdown of n-hexadecane an equimolecular mixture of alkane and alkene must be formed.

EXPERIMENTAL

Experiments on the catalytic aromatization of n-hexadecane were carried out at atmospheric pressure in an apparatus of the circulating type which has previously been described by one of us along with the method of operation [3]. The molybdenum catalyst used was that which is employed in the DVD process with a MoO_3 content of 8% [4]. 60 ml of catalyst was loaded into the reactor. Regeneration of the catalyst was carried out by blowing through air at 520°. As the starting material n-hexadecane was used which had physical constants agreeing with the data in the literature [5].

Fractional distillation of the combined catalyzate from a series of experiments conducted under identical conditions was carried out on a rectifying column with an efficiency of 22 theoretical plates. The separation of fractions up to 200° was carried out at atmospheric pressure; above 200° the fractions were taken in vacuo at a residual pressure of 30 mm.

Quantitative determination of the aromatic hydrocarbon content of the fractions of the catalysate boiling up to 200° was carried out by an optical method, employing the specific [6] and relative [7] dispersion. The deviation in the determination by the two methods did not exceed 1%. Determination of the indices of refraction (n_D, n_C, n_F) was carried out with a Pulfrich refractometer at 20°. The aromatic hydrocarbon content in the catalyzate fractions with a boiling point higher than 200° was determined by the method of sulfonation with subsequent recalculation of the volumetric precentages to the weight basis. Gas analysis was carried out in a VTI apparatus.

Identification of the aromatic hydrocarbons in the catalysate fractions boiling up to 200° and above was carried out by the method of Khodzhaev and Ibragimov [8] with a few changes. The presence of benzene in the

fractions 75-85° was established by the formolite test [9] and by nitration [10]; toluene was identified in the fraction 105-115° by nitration [11].

SUMMARY

1. It has been established that n-hexadecane can be easily transformed by conversion over a molybdenum catalyst into aromatic hydrocarbons boiling over a wide temperature range.

2. A scheme has been proposed for the conversion of n-hexadecane over a molybdenum catalyst.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

XIII. REACTION OF 1-PHENYL-4-METHYLCYCLOHEXANO HEXANOL WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

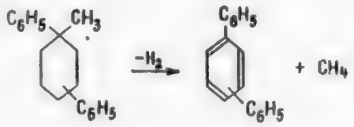
N. G. Sidorova and I. A. Tushinskaya

The character of the isomerization of radicals in the cycloalkylation of aromatic compounds with cyclohexane derivatives in the presence of aluminum chloride depends upon the nature of the substituents in the molecule of the cyclic compound. In the presence of a methyl group the aryl group tends to attach to the same carbon atom, but under mild conditions it is possible to partially carry out the reaction without isomerization [1]. When benzene is alkylated with 1-phenylcyclohexanol [2], 1, 2-dihalogenocyclohexanes [3], or 4-chlorocyclohexanol [4] the phenyl groups always go on to the 1, 3 or 1, 4 positions of the cyclohexane ring regardless of the conditions and the initial position of the functional groups. Moreover, in the latter reactions a considerable quantity of reduction products is always formed.

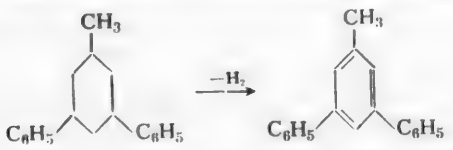
It was of interest to ascertain how the simultaneous presence of a methyl and a phenyl group would affect the course of the alkylation reaction. For this purpose we investigated the reaction between 1-phenyl-4-methylcyclohexanol and benzene in the presence of $AlCl_3$. The reaction proceeded easily with the formation of both an alkylation product and a reduction product. The yields of these varied somewhat depending on the quantity of $AlCl_3$ used, but the reduction product always predominated. It consisted of two hydrocarbons — 1-methyl-3--phenyl- and 1-methyl-4-phenylcyclohexane — as was shown by their dehydrogenation to the corresponding methyldiphenyls and oxidation of the latter to the phenylbenzoic acids.

The alkylation product was a viscous, fluorescent liquid, and in only two condensations with a large amount of $AlCl_3$ there was isolated a trifling quantity of a crystalline hydrocarbon with m.p. 149°, which was not investigated. Upon dehydrogenation of the liquid three hydrocarbons were obtained — m-terphenyl (little), p-terphenyl, and a hydrocarbon with m.p. 132° (main product), which was identified by a mixed melting point test with 1--methyl-3, 5-diphenylbenzene synthesized by the condensation of toluene with cyclohexanol and dehydrogenation of the dicyclohexyltoluene obtained.

The terphenyls could be produced only by dehydrogenation with splitting off of the methyl group from the quaternary carbon atoms of 1-methyl-1, 3-diphenyl- and 1-methyl-1, 4-diphenylcyclohexanes.

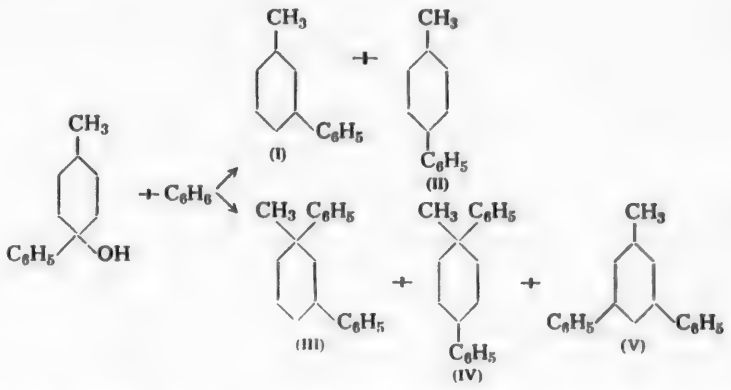


1-Methyl-3, 5-diphenylbenzene could be obtained both from 1-methyl-3, 5-diphenylcyclohexane,



and from 1-methyl-1, 3-diphenylcyclohexane as a result of dehydrogenation with migration of the methyl group. However, the fact that dehydrogenation occurred stepwise, first with the formation of 1-methyl-3, 5-diphenylbenzene and then with the production of terphenyl, indicates that 1-methyl-3, 5-diphenylcyclohexane was present in the reaction mixture.

Thus, the reaction of 1-phenyl-4-methylcyclohexanol with benzene in the presence of aluminum chloride goes according to the scheme



In all the alkylation products (III, IV, and V) the phenyl groups were in the 1,3 or 1,4 positions to each other, i.e., they were located the same as in the condensation products of 1-phenylcyclohexanol, 1,2-dichlorocyclohexane, and 4-chlorocyclohexanol with benzene. Consequently, the character of the effect of the phenyl group is preserved even in the presence of the methyl group in the substituted cyclohexanol. But the effect of the methyl group in this case is less and in only an insignificant part of the alkylation products (III and IV) are the methyl and the phenyl groups on the same carbon atom, while the chief product (V) has a symmetrical structure, which explains its predominant formation.

EXPERIMENTAL

Synthesis of 1-phenyl-4-methylcyclohexanol [5]. 4-Methylcyclohexanol was prepared by the hydrogenation of p-cresol in the presence of Raney nickel at 180° and 100 atm. hydrogen pressure. B. p. 166-167° (720 mm). Its oxidation with sodium bichromate and sulfuric acid yielded 4-methylcyclohexanone (yield 84%). B. p. 167-169° (715 mm). From the latter, 1-phenyl-4-methylcyclohexanol was prepared by a Grignard reaction with C_6H_5MgBr. Yield 64%. B. p. 142-144° (13 mm), n_D^{20} 1.5345.

Reaction of 1-phenyl-4-methylcyclohexanol with benzene in the presence of $AlCl_3$ was carried out in a three-necked flask with mechanical stirring. To a mixture of 19 g (0.1 g-mole) of the alcohol and 200 ml (2.2 g-mole) of benzene was added in small portions $AlCl_3$, the quantity of which varied in different experiments from 12 g (0.09 g-mole) to 20 g (0.15 g-mole). The time for the addition of the $AlCl_3$ varied from 1 to 15 hours, but it did not appreciably affect the yields. After all the $AlCl_3$ was added, the mixture was allowed to stand at room temperature until the next day and it was then heated, first at 50-55° and afterwards to boiling for several hours. The duration of heating also had little effect on the yields and 2 hours was completely sufficient. The mixture was then decomposed with dilute hydrochloric acid, washed several times with water, dried over $CaCl_2$, and distilled. The following fractions were separated: 1st, methylphenylcyclohexanes with b.p. 122-125° (15 mm); 2nd, methyldiphenylcyclohexanes with b.p. 160-200° (5 mm).

Depending on the amount of $AlCl_3$ used for the reaction, both the general yield and the yield of the separate fractions varied. The best results were obtained with 0.12-0.15 g-mole of $AlCl_3$. In this case the yield of methylphenylcyclohexanes was 48-49%, and the yield of methyldiphenylcyclohexanes was 30-32%.

The methylphenylcyclohexane fraction was contaminated with cycloolefines, from which it was freed by repeated treatment with sulfuric acid. After this it was washed with water and the product was dried over calcium

chloride and distilled over sodium. A mixture of 1-methyl-3-phenyl- and 1-methyl-4-phenylcyclohexanes was obtained:

b.p. 112-113° (10 mm), d_4^{20} 0.9471, n_D^{20} 1.5285; MR_D 56.67; calc. 56.43.

Found %: C 89.86; H 10.25. $C_{13}H_{18}$. Calculated %: C 89.59; H 10.41.

Dehydrogenation of methylphenylcyclohexanes. 2 g of the hydrocarbons was heated for 40 hours in a sealed tube with 1.5 g of selenium at 300-370°. The tube was periodically opened to remove the hydrogen selenide. The dehydrogenation product was extracted with benzene and after removal of the solvent was distilled over sodium. A mixture of m- and p-methyldiphenyls was obtained. B. p. 153-155° (25 mm), n_D^{20} 1.6044. In a freezing mixture the product partially crystallized.

Dehydrogenation over platinized carbon in an open tube at 250-280° proceeded slowly and was not complete after 80-100 hours. A product was obtained with b.p. 100-110° (6 mm), n_D^{20} 1.5850.

Identification of methyldiphenyls. Oxidation was carried out with a 2% solution of $KMnO_4$ while heating on a water bath for 30 hours with mechanical stirring [6]. A mixture of acids was obtained with m.p. 160-180°. From it was separated by fractional crystallization from 50% alcohol, p-phenylbenzoic acid as needles with m.p. 224°. It was not possible to separate pure m-phenylbenzoic acid by crystallization – a product was obtained with m. p. 160-162°. Therefore the mixture remaining after the removal of the p-phenylbenzoic acid was separated through the barium salts. For this purpose the alcoholic mother liquors were treated with barium hydroxide to a neutral reaction. The barium salt of p-phenylbenzoic acid that precipitated was filtered off and the free acid was isolated from it by acidification. m-Phenylbenzoic acid was obtained from the filtrate, after evaporation and acidification, as leaflets with m.p. 165° (from alcohol).

According to the data in the literature [7] p-phenylbenzoic acid melts at 224° and m-phenylbenzoic acid at 166°.

p-Phenylbenzoic acid was obtained in an amount approximately 3 times greater than m-phenylbenzoic acid. o-Phenylbenzoic acid was not detected.

m-Methyldiphenyl was identified by nitration [8]. 12 ml of nitric acid (d 1.4) was added dropwise with vigorous shaking to 0.8 g of methyldiphenyls. The reaction mixture was then heated on a hot water bath for 15 minutes, after which it was cooled and poured into ice. The precipitate that separted was washed several times with water and recrystallized from alcohol. After repeated crystallization 4,4' - dinitro-m-methyldiphenyl was obtained with m.p. 195°. A mixed melting point test with a known sample of 4,4' - dinitro-m-methyldiphenyl (m.p. 196°) gave no depression.

The methyldiphenylcyclohexane fraction was purified by repeated distillation over sodium. A very viscous, light yellow liquid was obtained.

B. p. 165-170° (3 mm), d_4^{20} 1.0252, n_D^{20} 1.5766, MR_D 80.83; calc. 84.76; EMR_D 3.93.

Found %: C 90.80; H 8.69. $C_{19}H_{22}$. Calculated %: C 91.14; H 8.86.

Dehydrogenation of methyldiphenylcyclohexanes in the presence of platinum. 6 g of the hydrocarbons was heated with 0.3 g of platinized carbon (20%) on a sand bath at 340-360° until crystals appeared (35-40 hours). Upon fractional distillation of the dehydrogenation product in vacuo, two fractions were obtained: 1st, b. p. 200--210° (23 mm), n_D^{20} 1.6066; 2nd, b. p. 180-190° (3.5 mm).

The 2nd fraction quickly started to crystallize. The crystals were pressed out on a porous plate and recrystallized from alcohol. 1-Methyl-3,5-diphenylbenzene was obtained as regular, quadrangular plates with m.p. 131-132°.

Found %: C 93.33, 93.44; H 6.66, 6.63. $C_{19}H_{16}$. Calculated %: C 93.40- H 6.60.

The 1st fraction was again dehydrogenated. Upon fractional distillation of the dehydrogenation product two fractions were separated: 1st, b. p. 160-170° (4 mm); 2nd, b. p. 195-200° (4 mm).

From the 2nd fraction were separated by crystallization from alcohol, 1-methyl-3,5-diphenylbenzene with m. p. 132° and p-terphenyl with m. p. 212°. A mixed melting point test with a known sample of p-terphenyl gave no depression.

The first fraction upon further dehydrogenation yielded p-terphenyl with m. p. 211°. A mixed melting point test with a known sample of p-terphenyl gave no depression.

In another experiment dehydrogenation was carried right to completion. After distillation of the reaction product and its crystallization from alcohol there were obtained m-terphenyl with m. p. 84°, 1-methyl-3,5-diphenylbenzene with m. p. 132°, and p-terphenyl with m. p. 211°. The crystals with m. p. 84° upon mixing with a known sample of m-terphenyl (m. p. 87°) melted at 85°.

Dehydrogenation in the presence of selenium. 2 g of methyldiphenylcyclohexanes and 1.5 g of selenium were heated in a hard glass test tube on a sand bath at 350-370°. The hydrogen selenide was absorbed in alkali. Heating was continued until coloration of the alkali ceased. The reaction product was extracted with benzene, washed with alkali, then with water, dried over calcium chloride, and distilled. Crystals of 1-methyl-3,5-diphenylbenzene with m. p. 131° precipitated from the product that distilled at 160-185° (7 mm). From the liquid portion after further dehydrogenation at 380° p-terphenyl was obtained with m. p. 208°.

Synthesis of 1-methyl-3,5-diphenylbenzene. 2.5 g of dicyclohexyltoluene (prepared from cyclohexanol and toluene by condensation with $AlCl_3$ [9]) and 0.4 g of 10% platinized carbon were heated in a hard glass test tube at 300-350° until the evolution of hydrogen and solidification of the mixture was finished. The product distilled at 195-199° (7 mm) crystallized at once. After recrystallization from alcohol, 1-methyl-3,5-diphenylbenzene was obtained in good yield as quadangular plates with m.p. 131-132°. A mixed melting point test with crystals of m. p. 131-132° obtained by dehydrogenation of methyldiphenylcyclohexane gave no depression.

Dehydrogenation with selenium also gave 1-methyl-3,5-diphenylbenzene with m.p. 131-132°.

According to data in the literature 1-methyl-3,5-diphenylbenzene melts at 130° [10].

SUMMARY

It has been shown that the reaction between 1-phenyl-4-methylcyclohexanol and benzene in the presence of aluminum chloride preoceeds in two directions: with the formation of reduction products — 1-methyl-3-phenyl- and 1-methyl-4-phenylcyclohexanes — and alkylation products — 1-methyl-1,3-diphenyl-, 1-methyl-1,4-diphenyl- and 1-methyl-3,5-diphenylcyclohexanes.

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CONDENSATIONS OF TRICHLOROETHYLENE WITH BENZENE

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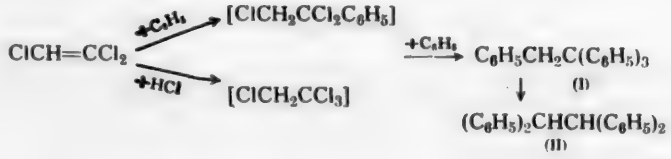
The present investigation was undertaken in connection with a study conducted in our laboratory on the alkylation of the aromatic nucleus with polyfunctional compounds. Such reactions are greatly dependent on the conditions under which they are carried out and they often are accompanied by anomalous processes [1].

In the condensation of trichloroethylene with benzene in the presence of $AlCl_3$ one would expect in the first stage either direct addition of a molecule of benzene or addition of HCl [2]; there further might occur substitution of chlorine atoms. The normal end product of the condensation might be unsymmetrical tetraphenylethane (I). However, under the influence of $AlCl_3$ it readily isomerizes to symmetrical tetraphenylethane (II) [3], which should be the principal product. We consider the following condensation scheme the most probable:



From the data in the literature it is evident that in the alkylation of benzene by tribromo- and trichloroethylene other products are obtained either wholly or in considerable amounts.

Anschutz [4] carried out condensations of tribromoethylene with benzene in the presence of $AlBr_3$. The reagents were used in the molar ratios 1 : 35 : 2.7, and the principal product proved to be 1,1-diphenylethylene. Moreover, triphenylmethane was formed, which Anschutz assumed might be a decomposition product of polyphenylethanes. The appearance of 1,1-diphenylethylene was explained by a poorly convincing scheme that assumed the splitting out of bromine from tribromoethylene.

Boeseken and Bastet [5] studied the reaction of trichloroethylene with benzene in the presence of mercuric chloride and aluminum. Tetraphenylethane (II) was obtained in 16% yield, and also 1,1,2-triphenylethane and 1,1-diphenylethane. The yields of the latter two compounds increased to 10-12% when the reaction mixture was heated. The authors considered that in the first stage the addition of benzene to trichloroethylene did not proceed according to Markovnikov's rule.

Recently the condensation of trichloroethylene with benzene in the presence of $AlCl_3$ was again studied by V. V. Korshak and K. K. Samplavskaya [6]. Only a tarry mixture of polyphenylalkanes was obtained, which was produced as a result of polycondensation of tetraphenylethanes with trichloroethylene. As a result of breaking up of the tar when it was distilled, diphenylmethane, triphenylmethane, and anthracene were formed. In the condensation scheme proposed it seemed to us that there were unsubstantiated assumptions concerning the direct replacement of the chlorine atoms of trichloroethylene by phenyl groups.

Proceeding from these literature data, we started to carry out the condensation of trichloroethylene with benzene under very mild conditions. Attempts to decrease the amount of $AlCl_3$ did not give positive results. A large excess of benzene was necessary to avoid tar formation. We carried out all our experiments with molar ratios of the reagents of 1 : 21 : 1. Then the condensation temperature was lowered. At 0° the symmetrical tetraphenylethane (II) was obtained, but in insignificant yield; at 12° the yield of it amounted to 32%, and at 30° it

reached 70% of theoretical. Further elevation of the temperature and also increasing the duration of the reaction from 4 to 64 hours led to a decrease in the yields of tetraphenylethane and accumulation of secondary products: diphenylmethane, dibenzyl, and 1,1,2-triphenylethane. Apparently, under the influence of $AlCl_3$ and benzene, even at 30°, decomposition of the symmetrical tetraphenylethane occurs. It has been noted [7] that dibenzyl is formed in considerable yield (54%) from tetraphenylethane in benzene solution in the presence of $AlCl_3$. In our experiments, carried out at 27°, diphenylmethane (20%) and dibenzyl (30%) were obtained from tetraphenylethane (II) in an excess of benzene under the influence of $AlCl_3$.

When we repeated the condensation of trichloroethylene with benzene under the conditions described by Korshak and Samplavskaya [6], we actually obtained a tarry mass. However, when it was treated with steam or extracted with alcohol, we succeeded in separating appreciable quantities of diphenylmethane and dibenzyl. In experiments with moist $AlCl_3$ a tar was obtained from which diphenylmethane, triphenylmethane, and anthracene were gotten by pyrolysis. In this case also half of the entire amount of diphenylmethane was separated by preliminary treatment with steam. There is no doubt that the course of the condensation of trichloroethylene with benzene is very highly dependent upon the conditions under which it is carried out (See table). Apparently symmetrical tetraphenylethane (II) is always formed, which undergoes decomposition in greater or less degree, even when its polycondensation with trichloroethylene occurs.

EXPERIMENTAL

Trichloroethylene was used which was obtained by the fractionation of a pure commercial preparation, B.p. 85-86° (730 mm), d_4^{20} 1.4376, n_D^{20} 1.4780.

The condensations were carried out in the usual apparatus with a stirrer. The trichloroethylene, dissolved in benzene, was added dropwise over the course of 2 hours to a mixture of benzene and $AlCl_3$; then the mixture was stirred for 2 hours more. The temperature was regulated if necessary by cooling or heating. In a number of cases the reaction mixture separated into two layers: the upper, orange-colored and the lower, dark brown. Decomposition was carried out with acidified ice water. When there were appreciable yields of tetraphenylethane (II), it separated as a crystalline, gray precipitate from the benzene layer in the separatory funnel. After the benzene layer was washed and dried, the benzene was distilled off; the crystalline and oily residues were separated by drawing the latter off with suction and were further purified by crystallization or distillation. When large amounts of tar were obtained, it was easily separated from the water and subjected either to treatment with steam or to extraction with alcohol. Typical experiments were repeated 3-4 times.

Condensations of Trichloroethylene with Benzene (Trichloroethylene 16 g, benzene 202 g, $AlCl_3$ 16 g; molar ratios 1:21:1; duration of reaction 4 hours)

Temperature	Yields (in %)				Tar (in g)	Remarks
	Tetraphenylethane	Triphenylethane	Dibenzyl	Diphenylmethane		
30°	70	—	—	—	3.7	—
30	26	7	11	5	4.0	Reaction was carried on for 64 hours
30	10	—	5	7	1.0	Reaction mixture was moistened with 0.5 ml of water
50	14	10	6	2	10.0	—
80	—	—	24	13	15.0	Benzene layer was steam-distilled
80	—	—	—	26	27.0	Reaction mixture was moistened with 0.5 ml of water; crude products were steam-distilled

Cleavage of tetraphenylethane (II). 10 g of (II) was dissolved in 100 g of benzene, then 8 g of $AlCl_3$ was added in portions (molar ratios 1:40:2). The mixture was left for 24 hours at 27°, and stirred from time to time. Two layers formed; the crude product separated after decomposition of the mixture with water was extracted with

hot alcohol. Upon cooling, dibenzyl precipitated with m.p. 50-52°, 1.6 g (30%)- from the mother liquor 2 g (20%) of diphenylmethane contaminated with dibenzyl was separated by vacuum distillation.

1,1,2,2-Tetraphenylethane (II). The crude condensation product melted at 201-206°. After 3 recrystallizations from benzene the m.p. was 209-210°[8]. A mixed sampel with a known preparation of symmetrical tetraphenylethane gave no depression in melting point.

1,1,2-Triphenylethane. This was separated from the fraction with b.p. 160-180° at 5 mm. Recrystallized from alcohol it melted at 54°. (Literature data: 54.5° [9]). A mixed sample with dibenzyl gave a sharp depression in melting point (25-30°).

Dibenzyl usually separated upon standing from the liquid fraction containing diphenylmethane (110-140° at 10 mm). Crystals from alcohol with m.p. 52°. Identical with a known preparation of dibenzyl.

Diphenylmethane [10]. This was separated by repeated distillation of the liquid fraction after the removal of dibenzyl.

B. p. 118-120° at 7 mm, d_4^{20} 1.0002, n_D^{20} 1.5702, MR_D 55.10; calc. 55.03.

By oxidation with chromic anhydride in acetic acid benzophenone was obtained with m.p. 47-48°; its semicarbazone melted at 165°.

SUMMARY

1. It has been established that 1,1,2,2-tetraphenylethane is formed in yields up to 70% of theoretical by the condensation of trichloroethylene with benzene at low temperatures (30°).

2. Under more severe condensation conditions there occurs, besides tar formation, the decomposition of tetraphenylethane to produce dibenzyl, diphenylmethane, and 1,1,2-triphenylethane.

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THE CONVERSION OF XYLENOLS BY ALUMINOSILICATE CATALYST*

1. THE CONVERSION OF 1,3,5-XYLENOL

N. N. Vorozhtsov, Jr. and V. N. Lisitsyn

The conversion of xylenols into phenol and cresols is interesting as a possible method for increasing the reserves of these valuable products. The present investigation was undertaken in order to obtain phenol and cresols by the dealkylation of xylenols by reacting them with benzene over an aluminosilicate catalyst. The coversion of xylenols on an aluminosilicate catalyst in the absence of benzene was also investigated.

When we commenced our investigations we had no knowledge of any papers on the conversion of homologs of phenol by an aluminosilicate catalyst. After we had succeeded in obtaining phenol, cresols and alkylbenzenes [1] by passing a mixture of xylenols (b.p. 210-225°) and benzene over an aluminosilicate catalyst, abstracts of patents were published, describing the dealkylation of homologs of phenol over an aluminosilicate catalyst [2] and also in the presence of an acid catalyst (concentrated sulfuric acid. dimethylsulfate) [3]. After we had completed our investigations, American authors published a study on the disproportionation of cresols and xylenols over an aluminosilicate catalyst [4].

The study of the conversion of 1,3,5-xylenol in a mixture with benzene over an aluminosilicate catalyst at 350-450° with a contact time of 22-87 seconds indicated that the reaction products contain phenol and all the isomers of cresol, together with neutral compounds with a b.p. above 100° and a small amount of water. A black carbonaceous deposit was precipitated on the catalyst. A small amount of gas, with hydrogen predominating, was liberated during the reaction.

Homologs of benzene – toluene, o,m-, p-xylenes, trimethylbenzenes (pseudocumene, mesitylene) and also durene – were isolated from the neutral substances, boiling above 100°.

More than half the neutral substances (58.5%) had boiling points above 200° (mainly between 270 and 370°).

When 1,3,5-xylenol was converted over aluminosilicate catalyst in the absence of benzene (at 350° with a contact time of 94.7 seconds) the reaction products contained phenol and all the isomers of cresol together with neutral compounds which commenced boiling at 115°. No toluene was found in the reaction products. A carbonaceous residue was deposited on the catalyst.

The conversion of xylenol is a purely catalytic reaction because when 1,3,5-xylenol is passed through a quartz tube filled with porcelain and glass at 400° with a contact time of 178 seconds 1,3,5-xylenol was recovered almost quantitatively.

The conversion of 1,3,5-xylenol in the presence of benzene proceeds differently than in the absence of the latter. The more fundamental conversion of the xylenol and the presence of toluene in the reaction products when the reaction is carried out in the presence of benzene indicate that in this case methylation of benzene takes place owing to demethylation of the xylenol.

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*From the candidate's thesis of V. N. Lisitsyn, defended in November 1954

EXPERIMENTAL

Initial Substances. 1,3,5-Xylenol—"pure" (Kharkov Chemical Reagent factory), b.p. 219.2° (756 mm); m.p. 63.5-64.0°. The benzene was obtained from commercial benzene by distilling the latter with a fractionating column. Solidification point 5.5°, d_4^{20} 0.880, n_D^{20} 1.4988. Commercial, petroleum-cracking aluminosilicate catalyst tablets (4 x 4 mm) were used as the catalyst. The bulk weight was about 0.54 kg/liter.

The experiments on the conversion of xylenols were carried out in an apparatus previously described [5]. The volume of the catalyst 65-68 cc. The initial substances were measured out from a buret. When the experiments were carried out with 1,3,5-xylenol in the absence of benzene, a buret with a jacket warmed by hot (90°) water was used The volumetric rate and the contact time were calculated by known formulas [6].

The catalyzate was treated with a 10% solution of caustic soda. The layer of aqueous alkali was separated, steam was blown through, and the phenols were precipitated by acidification with concentrated sulfuric acid. The layer of phenols was separated, and the aqueous layer extracted with ether. After distillation of the ether, the residue was added to the layer of phenols. The neutral reaction products which were insoluble in alkalies were dried with calcium chloride. The phenols and neutral substances were distilled from a flask with a rectifying column [7]. The amount of residue on the catalyst was estimated from the increase in weight of the latter. The period of operation of the catalyst was not more than 3 hours, after which time the catalyst was regenerated by heating in a current of air to 500-550° for 2.5-3 hours.

The conversion of a solution of xylenol in benzene over aluminosilicate catalyst. During 34 experimental cycles (3 hours each) a solution of 527.1 g (4.31 moles) of 1,3,5-xylenol in 1902.5 g (24.4 moles) of benzene was passed over the catalyst at 400°. The contact time was 37.1 seconds. The increase in weight of the catalyst was 91.7 g (17.4%)*.

137.2 g (26.1%) of phenols, 1756.6 g of unchanged benzene (92.3 % of the amount taken) and 223.3 g (42.4%) of neutral substances boiling above 100°, were obtained by treating the catalyzate (2299.3 g). The following fractions were obtained by distilling the phenols at 4 mm: 1st fraction b.p. 60-64°, 0.8 g (0.2 %); 2nd b.p. 64-67°, 26.0 g (4.9 %); 3rd b.p. 67.75°, 32.2 g (6.2 %); 4th b.p. 75-77°, 22.2 g (4.2 %); 5th b.p. 77-81°, 5.8 g. (1.1 %).

When the residue was distilled at atmospheric pressure the following fractions were obtained: 6th b. p. 215--220°, 20.0 g (3.8%); 7th b.p. 220-226°, 15.5 g (2.9%); residue and losses 14.7 g (2.8%).

The absorption spectra in the ultraviolet regions were taken from the 1st and 4th fractions and the presence of the following compounds was established: in the 1st fraction — phenol (absorption λ_{max} 2637 and 2751 A), o-cresol (λ_{max} 2747 A), traces of m-cresol (λ_{max} 2788 A); in the 2nd fraction—phenol (λ_{max} 2636 and 2751 A), o-cresol (λ_{max} 2746 A), m-cresol (λ_{max} 2779 A), p-cresol (λ_{max} 2831 A); in the 3rd fraction — p-cresol (λ_{max} 2830 A), traces of m-cresol (λ_{max} 2779 A) and o-cresol (λ_{max} 2639 and 2746 A); in the 4th fraction — p-cresol (λ_{max} 2830 A).

The m-cresol contents in the 2nd fraction (9.2%) and the 3rd (65.7%) were determined by Raschig's method.

A crystalline residue, which on nitration gave picric acid with m.p. 118-119°, was separated from the 2nd fraction by cooling to 0°. A mixed melt of this acid with pure picric acid had m.p. 119-120°. From the picric acid produced, the naphthalene picrate was obtained in the form of yellow needles with m.p. 148°. According to data in literature the m.p. of naphthalene picrate is 149.5°.

The following fractions were obtained by distillation of the neutral substances: 1st fraction b.p. 100-113°, 22.0 g (4.2%); 2nd b.p 113-133°, 6.1 g (1.1%); 3rd b.p. 133-142°, 39.8 g (7.6%); 4th b.p. 142-166°, 2.5 g (0.5%); 5th b.p. 166-175°, 21.9 g (4.2%); 6th b.p. 185-200°, 7.0 g (1.3%); the residue was 124.0 g (23.5%).

0.2 g of the 1st fraction, containing toluene, was nitrated with nitric acid [9]. 0.32 g of pale yellow needles with m.p. 70.2-70.4° (from diluted ethyl alcohol) was obtained. The mixed melting point with 2,4-dinitrotoluene showed no depression.

0.30 g. of pale yellow needles with m.p. 181.5-182° (from ethyl alcohol plus a small amount of benzene) was obtained on nitration of 0.33 g of the 3rd fraction.

* Here and subsequently in the text, unless otherwise stated, the percentages given are of the amount of initial xylenol.

The oxidation of 1.5 g of the 3rd fraction by potassium permanganate, the separation of the mixture of acids and the production of their diethyl esters were carried out according to the method of B. L. Moldavsky and his co-workers [11]. Phthalic anhydride with m.p. 129.5-130.5° (m.p. given in literature: 131.6°) was obtained. 0.65 g of tetraphthalic acid and 0.53 g of isophthalic acid were isolated from the mixture of acids (1.70 g). The dimethyl ester of tetraphthalic acid with m.p. 139-140° (m.p. given in literature: 141-142°, 140.5-141.0°) and the dimethyl ester of isophthalic acid with a m.p. of 61-62° (m.p. given in literature: 64-65°) were also obtained. The mixed melting points of these with the known pure compounds showed no depression.

0.3 g of trinitropseudocumene in the form of pale yellow prisms with a m.p. of 184.5° (from ethyl alcohol) was obtained by the nitration of 0.5 g of the 5th fraction; the m.p. given in literature is 185°. The mixed melting point with pure trinitropseudocumene showed no depression.

Found %: N 16.59, 16.82. $C_9H_9O_6N_3$. Calculated %: N 16.47.

In addition, pseudocumene-5-sulfonic acid was obtained by sulfonation [12] of the 5th fraction: it was in the form of white platelets with m.p. 109-110° (from 20% hydrochloric acid). The mixed melting point with pure pseudocumene-5-sulfonic acid showed no depression.

1,3,5-benzenetricarbonic acid with m.p. 364° was obtained together with 1,2,4-benzenetricarbonic (trimellitic) acid by the oxidation of the 5th fraction. When the former was treated with an ethereal solution of diazomethane the trimethyl ester with m.p. 141.5° was obtained. The melting points given in literature for these acids are 375-380° and 345-350°, respectively; that for the trimethyl ester is given as 141-144°.

When the 6th fraction was cooled to 0° 1,2,4,5-tetramethylbenzene (durene) was obtained in the form of white leaflets with a m.p. of 78.0-78.5°.

Found %: C 89.50, 89.61; H 10.82, 10.97. $C_{10}H_{14}$. Calculated %: C89.49, H 10.51.

The mixed melting point with pure durene showed no depression. The m.p. given in the literature is 80°.

The conversion of 1,3,5-xylenol by aluminosilicate catalyst. 35.9 g (0.29 mole) of 1,3,5-xylenol was passed over 35 g of catalyst for 2 hours 40 minutes at 350°. The contact time was 94.7 seconds. The addition in weight of the catalyst was 4.9 g (13.6%). Treatment of the catalyst gave 17.9 g (49.8%) of phenols (without extraction of the phenols from the aqueous layer) and 6.2 g (17.2%) of neutral substances. The following fractions were obtained by distillation of the phenols: 1st fraction 180-203°, 0.7 g (1.9%)- 2nd b.p. 203-210°, 1.1 g (3.1%); 3rd b.p. 210-225°, 9.2 g (25.6%); the residue and losses were 6.9 g. The m-cresol content, determined by Raschig's method [8], in the 1st fraction was found as 60.2% and 59.0% (mean value 59.6%).

Distillation of the neutral substances gave the following fractions: 1st fraction b.p. 115-150°, 0.9 g (2.5 %); 2nd b.p. 150-180°, 0.7 g (1.9 %); residue 4.6 g (12.8 %). The 1st fraction was nitrated by nitric acid [9]. Pale yellow needles with a m.p. of 179° were obtained. The mixed melting point with 2,4,6-trinitro-m-xylene (m.p. 182°) showed no depression.

Conversion in the absence of catalyst. 28.6 g (0.235 mole(of 1,3,5-xylenol was passed through a tube filled with porcelain and glass for 4 hours at 400°. Distillation of the catalyzate (27.4 g) gave 26.7 g of the initial 1,3,5-xylenol with a b.p. of 219-220° (m.p. 63°).

SUMMARY

1. When xylenol and benzene in ratios of 1:2 or 1:4 (by weight) are passed over aluminosilicate catalyst at 350-450° (contact time of 22-110 seconds) phenol and o-, m- and p-cresols are formed. Homologs of benzene (toluence, o-, m- and p-xylenes, pseudocumene, mesitylene, durene) and neutral compounds with b.p. above 185° are formed simultaneously, the amounts formed being up to 30% and 29% of the weight of the xylenol, respectively.

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** In Russian.
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THE INITIATORY ACTIVITY OF 1,1-DIPHENYLETHANE HYDROPEROXIDE IN THE EMULSION AUTOXIDATION OF A HYDROCARBON

R. V. Kucher, V. D. Enalyev and A. I. Yurzhenko

The interest in organic peroxides results from the fact that they are formed as intermediate products during the oxidation of various compounds [1]. By studying methods of obtaining these compounds and also their stability, we can shed light on the mechanisms of the corresponding reactions. In addition, the study of peroxides and hydroperoxides is very important from a practical point of view, since these compounds are the initiators of many chemical processes – in particular, the very important process of polymerization [2]. In this instance, the activity of peroxide compounds is determined to a considerable extent by their thermal stability. The latter depends, in turn, on many factors such as the structure of the peroxide molecule, the medium, various addition agents, etc.

Hydroperoxides containing a tertiary crabon atom in their molecule are of particular interest because they are obtained comparatively easily by the autoxidation of the corresponding hydrocarbons. In this instance, the initial point of attack is the tertiary carbon atom itself [1]. T. I. Yurzhenko and his co-workers prepared a number of hydroperoxides of this type, with various structures [3]; they showed that the thermal stability of these compounds depends on the nature of the substituents at the tertiary carbon atom. These authors also carried out investigations on the initiatory activity of tertiary hydroperoxides in the mass polymerization of styrene [4]. In this instance, 1,1-diphenylethane hydroperoxide shows particularly high activity. During polymerization in emulsions, the activity of tertiary hydroperoxides depends on their phase distribution [5]. Although the fact is undoubtedly of primary importance during reactions in emulsions, the quantitative aspect of this process has not received the attention it merits. It may be assumed that the phase distribution of the hydroperoxide is governed to a considerable extent by the presence of the colloid electrolyte (the emulsifier) which makes the conjugated solution of the hydroperoxide possible.

For this reason we consider the quantitative investigation of the distribution of tertiary hydroperoxides and, in particular, 1,1-diphenylethane hydroperoxide (DPH) between the aqueous and hydrocarbon phases to be of interest in connection with the thermal stability of the hydroperoxide. The study of these problems is important not only in the use of DPH as the initiator of emulsion polymerization, but also in the synthesis of a hydroperoxide by the autoxidation of the initial hydrocarbon in emulsions.

The object of the present work is the investigation of the thermal decomposition and also the phase distribution of 1,1-diphenylethane hydroperoxide in various media in connection with the initiatory activity of hydroperoxide in the autoxidation of the initial hydrocarbon in emulsions.

The experiments were carried out both with and without emulsifiers. The 1,1-diphenylethane hydroperoxide was obtained by the autoxidation of 1,1-diphenylethane in a homogeneous medium with molecular oxygen at 80° and up to 30-35 % of peroxide. The initial hydrocarbon was synthesized by the condensation of styrene with benzene in the presence of sulfuric acid, using the method of T. I. Yurzhenko and N. V. Arefyev [6].

A solution of 160 cc of styrene in 400 cc of benzene was added dropwise (over a period of 4 hours) to a mixture of 1400 cc of benzene and 160 cc of sulfuric acid, with vigorous stirring. The reaction was carried out at room temperature. The hydrocarbon layer was neutralized by solid caustic soda, and then the benzene was distilled off. The hydrocarbon was distilled under vacuum (12.5 mm). Treatment with solid alkali (instead of washing with water as recommended by the authors) makes it possible to avoid the formation of an emulsion which results in high losses. The fractions with a b.p. of 135.5-136.5° were selected for the investigation. They hydro-

carbon obtained was washed repeatedly with concentrated sulfuric acid, a 10% solution of caustic soda, water, and then was dried. The purified hydrocarbon thus had constants corresponding to the data given in literature and was not decolorized by the action of potassium permanganate solution.

The hydroperoxide obtained by the oxidation of 1,1-diphenylethane is a white crystalline substance with an m.p. of 82° easily separated, by cooling, from the hydrocarbon undergoing oxidation. A 100% pure product is obtained after recrystallization from petroleum ether. It may be pointed out that the readiness with which the hydroperoxide is isolated in the pure form justifies the assumption that its preparation in this manner offers prospects of a practical application in industry.

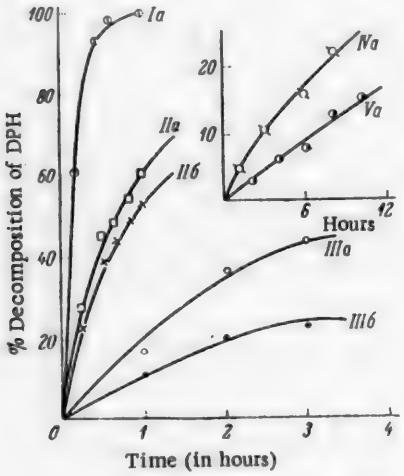

Fig. 1. Kinetic curves of the decomposition of DPH at 98.5° (a) and 80° (b) in aqueous solutions (pH 9.9). In the presence of: I) 2% leucanol, II) 2% potassium palmitate, III) 2% Nekal and in 1,1-diphenylethane (IV); V) curve of the decomposition of cumene hydroperoxide in cumene.

In order to characterize the initiatory activity of DPH in reactions taking place in emulsion systems, we investigated the thermal decomposition of the hydroperoxide both in a hydrocarbon medium and in a 0.1 N aqueous solution of sodium carbonate (pH 9.9) in the presence of emulsifiers. These experiments were carried out in sealed ampoules in an atomosphere of nitrogen in a thermostat at a suitable temperature. The amount of hydroperoxide was determined iodometrically [7]. The results obtained are given in Fig. 1. It follows from these data that in a hydrocarbon medium DPH is less thermally stable than isopropylbenzene hydroperoxide (the data for which are given for purposes of comparison). As regards the aqueous phase, the thermal decomposition of DPH also takes place far more rapidly than cumene hydroperoxide. This is in agreement with, and complements, the data on the thermal stability of the tertiary hydrocarbons obtained by T. I. Yurzhenko and his co-workers [3]. It may also be pointed out that the thermal decomposition of 1,1-diphenylethane hydroperoxide in an aqueous alkaline medium in the presence of emulsifiers proceeds far more rapidly than in the hydrocarbon phase. The experiments were not carried out in an aqueous medium in the absence of emulsifiers because of the negligible solubility of the DPH. When DPH was used as an initiator of reactions it was, therefore, to be expected that initiation takes place simultaneously in the aqueous phase. This fact is of great importance for explaining the mechanism of emulsion polymerization of hydrocarbons and also oxidation reactions of hydrocarbons in emulsions, the study of which we are undertaking.

The acceleration of the decomposition of DPH in the aqueous phase plays a vital part when this reaction is carried out in the presence of both the hydrocarbon and the aqueous phase (in emulsion). This is confirmed by corresponding experiments on the decomposition of DPH carried out in emulsions of 1,1-diphenylethane in aqueous solutions of Na_2CO_3 at a pH of 9.9 with a phase ratio of 1:1 (Fig. 2). It follows from these data that in the presence of the aqueous phase the decomposition of DPH is considerably accelerated, other circumstances being equal. In this case the nature of the decomposition, in our opinion, is as follows. The major decomposition of the DPH

$$ROOH \rightarrow R\dot{O} + \dot{O}H \qquad (1)$$

takes place in the aqueous phase. In the hydrocarbon phase the hydroperoxide is far more thermally stable. Because of the limited solubility of the hydroperoxide in water ($2.75 \cdot 10^{-4}$ moles/liter at 20°) the major proportion of it is, however, in the hydrocarbon phase. In the case of the thermal decomposition of DPH in an emulsion the oleophase is, therefore, a somewhat unusual "reserve" of hydroperoxide. The DPH therefore enters the aqueous phase, where its major decomposition takes place. In this connection the aqueous phase must be considered as the main source of the generation of free radicals during the thermal decomposition of DPH in emulsions.

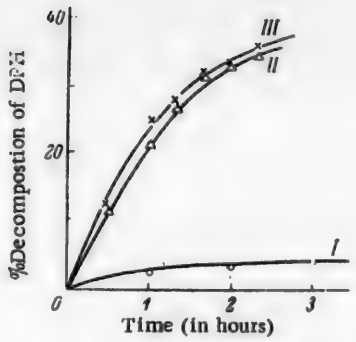

Fig. 2. Kinetic curves of the decomposition of DPH at 70° in 1,1-diphenylethane (I) and alkaline emulsions in the presence of 2% leucanol (II) and the absence of emulsifiers (III).

Proceeding from the fact that we consider the phase distribution of the hydroperoxide to be of very great importance during the initiation of reactions in emulsions, we carried out investigations on the distribution coefficient $K = C_1/C_2$ between the hydrocarbon phase (1,1-diphenylethane) and aqueous solutions of emulsifiers. In this equation, C_1 and C_2 are the concentrations of the hydroperoxide in the aqueous and hydrocarbon phases.

Table 1 gives the relationship of the distribution coefficient of DPH between the oleophase (1,1-diphenylethane) and an aqueous solution of sodium carbonate (pH 9.9) at various contents of two colloidal electrolytes, Nekal and potassium palmitate.

With increasing concentration of the emulsifier (C_e) the hydroperoxide passes increasingly into the aqueous phase; this fact is more pronounced in the case of potassium palmitate than with Nekal. This fact must be associated with the presence of conjugated solution of DPH in aqueous solutions of colloidal electrolytes, which is determined, in turn, by the degree of "colloidicity" (micelle formation) of the emulsifier. The transition of the hydroperoxide into the aqueous phase is very important, particularly in the case of such virtually water-insoluble compounds as DPH.

Distribution Coefficient of DPH Between a 0.1 N Aqueous Solution of Na_2CO_3 and 1,1-Diphenylethane

In the presence of			
Nekal		Potassium palmitate	
C_E (%)	K	C_E (%)	K
1.0	0.0043	0.5	0.0052
2.0	0.0132	1.0	0.0112
3.0	0.0181	2.0	0.0187
5.0	0.0288	3.0	0.0290

The use of a colloidal electrolyte (emulsifier) therefore assists the generation of free radicals in the aqueous phase during thermal decomposition of the hydrogen peroxide as a result of its passing into the aqueous phase. This must undoubtedly influence the initiatory activity of DPH when carrying out reactions in emulsions. This influence is quite evident in the comparison of the data obtained on the rate of autoxidation of 1,1-diphenylethane in emulsions both in the presence and absence of emulsifiers (Fig. 3).

The oxidation of the hydrocarbon was carried out in glass flasks with a reflux condenser, the oxygen being bubbled through at a rate of 20 cc/min. The reaction mixture was mixed by means of a recycling stirrer which provides the most efficient contact of oxygen with the liquid. The kinetic experiments were carried out at 80° and with a phase ratio by volume (hydrocarbon : aqueous phase) of 1:4 in the presence of 0.1 g-equiv./liter of Na_2CO_3 in the aqueous phase.

It may be pointed out that the rate of accumulation of hydroperoxide during the oxidation of 1,1-diphenylethane was less than during the oxidation of isopropylbenzene. The relative capacity of these hydrocarbons to undergo oxidation remains the same when passing from oxidation in a homogeneous medium to oxidation in an emulsion. In addition, in the presence of an aqueous solution of alkali the yield of DPH with time also increases

in comparison with the oxidation of a hydrocarbon in a homogeneous medium (Fig. 3). Other authors have noted a similar phenomenon during the oxidation of isopropylbenzene [8] and p-cymene [9]. After the separation of the hydrocarbon phase the DPH separates out in the pure form just as readily as in the case of mass oxidation.

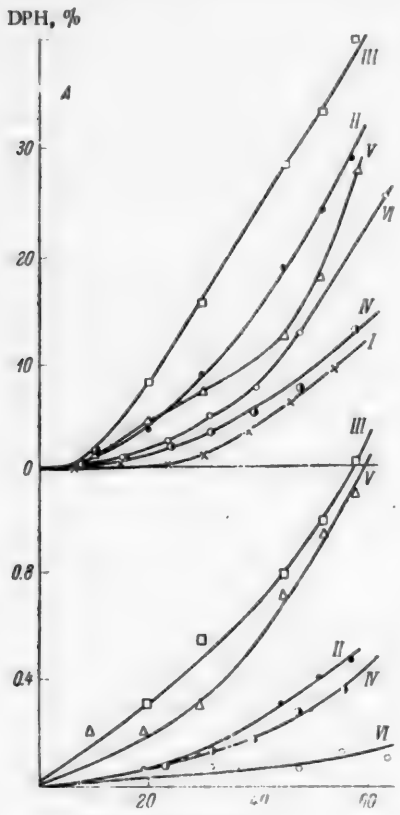

Fig. 3. Curves of the yield of DPH during the oxidation of hydrocarbon at 80°.
In a homogeneous medium (I) and in alkaline emulsions in the presence of: II) 2% leucanol; III) 2% potassium palmitate; IV) 2% Nekal; V) 5% Nekal; VI) in the absence of emulsifier:
A) hydrocarbon phase, B) aqueous phase.

The rate of accumulation of hydroperoxide during the oxidation of 1,1-diphenylethane in an emulsion increases considerably as a result of the introduction of emulsifiers (potassium palmitate, leucanol). The increase in the rate of accumulation takes place largely as a result of a decrease in the induction period (particularly in the presence of potassium palmitate). The stability of the emulsion during oxidation decreases with time (16-20 hours from the commencement of the reaction). There is a simultaneous increase in the DPH content in the aqueous phase. This increase occurs as a result of the increase of the distribution coefficient of the hydroperoxide in the presence of emulsifiers.

When Nekal is used at concentration of 2 % as the emulsifier a decrease in the rate of accumulation of DPH in the aqueous phase is observed. When a 5 % solution of this emulsifier is used, however, the rate of autoxidation of 1,1-diphenylethane in the emulsions increases in comparison with the reaction rate in the absence of an emulsifier.

The explanation of the acceleration of the autoxidation of 1,1-diphenylethane in emulsions must take into account the fact, which we noted, of an increase in the distribution coefficient and also the acceleration of the decomposition of the hydroperoxide in the aqueous medium compared with the hydrocarbon phase. In the presence of leucanol, and also of potassium palmitate, the decomposition of the hydroperoxide [reaction (1)] is much faster in the aqueous phase than in the hydrocarbon phase. Since (as we established) the aqueous phase contains up to 2 % of conjugated solution of 1,1-diphenylethane, the formation of free radicals according to the system

$$\dot{RO} + RH \rightarrow ROH + \dot{R} \qquad (2)$$

is considerably assisted.

On the other hand, the presence of an emulsifier in the aqueous phase increases the solubility of oxygen, as was proved by us in further experiments. The free radicals $\dot{R}$ subsequently interact with the oxygen, forming hydroperoxides. As a result of the low coefficient of distribution, the accumulating DPH then passes into the hydrocarbon phase where the thermal decomposition of the hydroperoxide takes place far more slowly. At the same time, the DPH, being surface-active, is adsorbed at the boundary of the distribution of the phases, thereby decreasing the mechanical strength of the adsorbed layer of emulsifier and thus reducing the stability of the emulsion. The retardation of the rate of oxidation in the presence of 2 % of Nekal occurs as a result of the lesser rate of thermal decomposition of DPH in the aqueous medium in the presence of this colloidal electrolyte compared with leucanol or potassium palmitate. An increase in the Nekal content results in an increase in the distribution coefficient and, therefore, in a greater number of free radicals which initiate the oxidation reaction.

All the above-mentioned evidence indicates that the role of the emulsifier in the oxidation of hydrocarbons

in emulsions cannot be considered to be merely a stabilizer of the emulsion. In such instances, the emulsifier is an essential kinetic factor having a definite influence on the rate and the topochemistry of the individual stages of the process.

SUMMARY

1. The rate of thermal decomposition of 1,1-diphenylethane hydroperoxide in a hydrocarbon medium and also in aqueous alkali was investigated. It was shown that hydroperoxide is thermally more stable in 1,1-diphenylethane than in an aqueous medium. The thermal decomposition of DPH is also accelerated in an alkaline emulsion of hydrocarbon.

2. The distribution coefficient of DPH between an aqueous solution of alkali and 1,1-diphenylethane is considereably increased in the presence of colloidal electrolytes (soaps), a fact which must be connected with the presence of a conjugated solution of hydroperoxide in the aqueous phase.

3. The liquid-phase oxidation of 1,1-diphenylethane by molecular oxygen in alkaline emulsions is accelerated in comparison with oxidation in a homogeneous medium. The nature of the emulsifier influences the process, the initiation of the reaction proceeding primarily in the aqueous phase.

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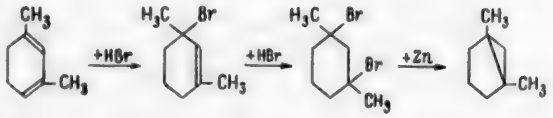
THE SYNTHESIS OF HYDROCARBONS

59. (0,1,3)-BICYCLOHEXANES WITH TWO QUATERNARY CARBON ATOMS

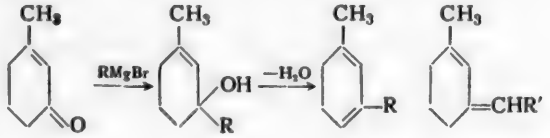
R. Ya. Levina, Kim Diai Gir, E. N. Smirnova, N. D. Orlova and E. G. Treshchova

In the previous paper [1], we described a new method for the synthesis of bicyclic "bridge" hydrocarbons of the (0,1,3)-bicyclohexane series with alkyl radicals at the carbon atoms connected with the "bridge". Hydrocarbons with this structure had not been described before in the literature. The method consisted in the exhaustive hydrobromination of the corresponding homologs of 1,3-cyclohexadiene with subsequent cyclization, by the action of zinc dust, of the cyclic ditertiary dibromides formed, for example

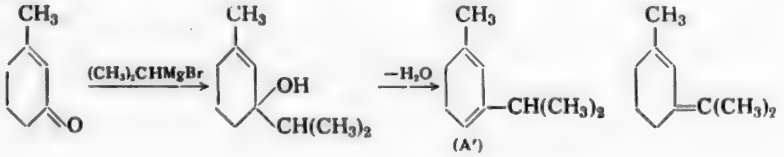


1,3-dimethyl- and 1,3,5-trimethyl-(0,1,3)-bicyclohexane were obtained from 1,3-dimethyl- and 1,3,5--trimethyl-1,3-cyclohexadiene.

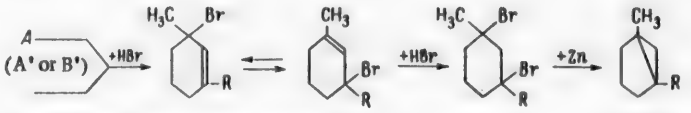
In the present investigations, other new hydrocarbons of the (0,1,3)-bicyclohexane series were synthesized by this reaction. The initial cyclic diene hydrocarbons were obtained as a mixture (boiling within a wide range) of two isomers with a different position of one double bond (A and B) by means of the interaction of 1-methyl--1-cyclohexen-3-one with alkylmagnesium bromide and subsequent dehydration (by distillation) of the tertiary cyclohenols formed.



In those reactions where the alkyl groups had an unbranched chain of carbon atoms (R = C_2H_5, C_3H_7, C_4H_9) the mixtures of diene hydrocarbons (A and B) were obtained with yields of 50-60 % and had closely similar refractive indices and specific gravities. When a tertiary alcohol containing isopropyl as the alkyl group was dehydrated, the yield of the mixture of diene hydrocarbons (A' and B') obtained was much less (19 %) and had far higher constants; this is explained by the predominant formation in this instance of a diene hydrocarbon with a semicyclic double bond (B')



By the addition of two molecules of hydrogen bromide to each mixture of diene hydrocarbons the corresponding ditertiary dibromides (1,3-dibrom-1-methyl-3-alkylcyclohexanes) were obtained and by the action of zinc dust in alcohol on the latter the homologs of (0,1,3)-bicyclohexane with two quaternary carbon atoms at the "bridge" were prepared:



(R = C_2H_5, C_3H_7, C_4H_9 and iso-C_3H_7) (I - IV)

The latter of these synthesized hydrocarbons (R = iso-C_3H_7) is isomeric with the dihydroterpene thujane included in the series of (0,1,3)-bicyclohexane, and is distinguished from it only by the position of the methyl group.

The presence of a three-membered ring in the bicyclic hydrocarbons obtained was confirmed by their Raman spectra. The yields of the hydrocarbons were from 7 to 30 %, calculated on the initial cyclic dienes; this low yield is caused by the fact that during the action of the zinc dust on the ditertiary 1,3-dibromide of the cyclohexane series, reduction and dehydrobromination processes [1] take place to a considerable extent as well as the Gustavson reaction; these lead to the formation of secondary reaction products, i.e. the initial cyclohexadienes and also cyclohexene- and cyclohexane hydrocarbons with the same alkyl groups.

The synthesized 1-methyl-3-alkyl-(0,1,3)-bicyclohexanes have a much lower boiling point than the secondarily formed homologs of cyclohexane, cyclohexene and cyclohexadiene (Table 1) and are, therefore, easily separated from the reaction products by fractional distillation.

EXPERIMENTAL

The initial 1-methyl-3-alkylcyclohexadienes (with an admixture in each instance of the isomeric 1-methyl-3-alkylidene-1-cyclohexene) were synthesized by the interaction of 1-methyl-1-cyclohexen-3-one* (b.p. 198-200°, n_D^{20} 1.4885 [2]) with alkylmagnesium bromides (with a ketone : alkylbromide : magnesium ratio of 1:1.3:1.3).

TABLE 1

Alkyl	Boiling point			
	1-methyl-3-alkyl-(0,1,3)-bicyclohexanes	1-methyl-3-alkylcyclohexanes (at 760 mm)	1-methyl-3-alkylcyclohexadienes (at 760 mm)	1-methyl-3-alkylcyclohexadienes (in mixture with 1-methyl-3-alkalidenecyclohexanes
C_2H_5 . .	133.5—134° (735.5 мм)	148.4—150° [4]	151.9—152.1°[4]	155—161° (745 мм)
C_3H_7 . .	155.5—157 (746 мм)	171.1—173 [4]	168—171 [6]	173—183 (760 мм)
C_4H_9 . .	179.5—179.8 (739 мм)	194.8—195.2 [4]	195.2—195.7 [4]	195—204 (742 мм)
Iso -C_3H_7 . .	150.5—150.6 (730 мм)	166—167 [5]	164—168 [7]	180—189 (742 мм)

The reaction was carried out with cooling by snow and salt and with stirring; the reaction mixture was then heated to boiling for 2-3 hours; decomposition was carried out by pouring on to ice and ammonium chloride. After con-

* Methylcyclohexenone is synthesized from acetoacetic ester via the intermediate stage of bis-methylene-acetoacetic ester [3]. Since the latter is partially decomposed during distillation, the yield of methylcyclohexenone, caluclated on the initial acetoacetic ester, is not more than 30%; this yield is increased to 50% if undistilled bis-methylene-acetoacetic ester is used.

ventional treatment of the ethereal solution and distillation of the ether the residue was distilled in a current of nitrogen (high-boiling polymers remained in the distillation flask), water being split off from the unsaturated tertiary alcohol. The dried mixture of dienes was again distilled in a current of nitrogen over sodium; a fraction with a wide boiling range was collected. The constants and yields are given in Table 2.

TABLE 2

1-Methyl-3-Alkyl-1,3-Cyclohexadienes in Mixture with 1-Methyl-3-Alkylidenecyclohexenes

Alkyl	Boiling point	n_D^{20}	d_4^{20}	Yield (%)
Ethyl	155—161°(745 mm)	1.4872	0.8472	62
Propyl	173—183 (760 mm)	1.4891	0.8488	58
Butyl	195—204 (742 mm)	1.4900	0.8478	47
Isopropyl	180—189 (742 mm)	1.5003	0.8699	19

The exhaustive hydrobromination of each mixture of diene hydrocarbons and the reaction of the 1,3-dibrom--1-methyl-3-alkylcyclohexanes formed with zinc dust (in 95 % ethyl alcohol) were carried out by methods previously described by us for the synthesis of 1,3-dimethyl-(0,1,3)-bicyclohexane [1]. The hydrocarbons obtained were washed free from alcohol and dried with calcium chloride, distilled over sodium and then fractionally distilled (over sodium). Judging from their Raman spectra the isolated homologs of (0,1,3)-bicyclohexane were either completely free from any admixture of unsaturated hydrocarbons (methylethyl- and methylisopropylbicyclohexane) or only contained traces – from 0.5 to 1 % – of them (methylpropyl- and methylbutylbicyclohexane).

The higher boiling hydrocarbon fractions were difficulty separable mixtures of close-boiling monocyclic hydrocarbons.

1-Methyl-3-ethyl-(0,1,3)-bicyclohexane. 14 g (30 %) of bicyclic hydrocarbon (1st fraction) with the following constants was obtained from 47 g of the mixture of dienes (A and B):

B.p. 133.5-134° (735.5 mm), n_D^{20} 1.4406, d_4^{20} 0.8165, MR_D 40.10. $C_9H_{16}\Delta$. Calculated: 40.06. Aniline point 33.7°

Found %: C 87.11, 86.94; H 13.02, 13.07. C_9H_{16}. Calculated %: C 86.93; H 13.07.

The following high-boiling fractions(at 735.5 mm) were collected:2nd fraction 3.3 g, b.p. 134-143°; n_D^{20} 1.4432; 3rd 5.5 g, b.p. 143-150°, n_D^{20} 1.4484; 4th 5 g, b.p. 150-151°, n_D^{20} 1.4540, d_4^{20} 0.8195 and residue 3 g, n_D^{20} 1.4802.

The constants of the 4th fraction had values close to the constants of 1-methyl-3-ethyl-3-cyclohexene: b.p. 151.9-152.1° (760 mm), n_D^{20} 1.4544, d_4^{20} 0.815 [4].

1-Methyl-3-propyl-(0,1,3)-bicyclohexane. 47 g (18 %) of methylpropylbicyclohexane was obtained (after repeated fractional distillation) from 264 g of a mixture of dienes (A and B):

B. p. 156.5-157° (746 mm), n_D^{20} 1.4445, d_4^{20} 0.8171, MR_D 44.98. $C_{10}H_{18}\Delta$. Calculated: 44.68.

Found %: C 86.68, 86.60; H 13.16, 13.31. $C_{10}H_{18}$. Calculated %: C 86.87; H 13.13.

It was not possible to separate the individual monocyclic hydrocarbons from the high-boiling fractions.

1-Methyl-3-butyl-(0,1,3)-bicyclohexane. 22 g (11 %) of methylbutylbicyclohexane (1st fraction) with the following constants was obtained (after repeated fractional distillation) from 195 g of the mixture of dienes (A and B):

B. p. 179.5-179.8° (739 mm), n_D^{20} 1.4471, d_4^{20} 0.8201, MR_D 49.62. $C_{11}H_{20}\Delta$. Calculated: 49.30.

Found %: C 86.41, 86.61, H 13.37, 13.47. $C_{11}H_{20}$. Calculated %: C 86.75; H 13.24.

The following high-boiling fractions (at 739 mm) were collected: 2nd fraction 3.6 g, b.p. 180-191.5°; 3rd 16 g, b.p. 192-194.5°, n_D^{20} 1.4523, d_4^{20} 0.8125; 4th 15 g, b.p. 194.5-197°, n_D^{20} 1.4633.

Judging by its constants the 3rd fraction contained principally 1-methyl-3-butyl-1-cyclohexene (data in literature [4] : b.p. 195.2-195.7° at 760 mm, n_D^{20} 1.4574, d_4^{20} 0.820).

1-Methyl-3-isopropyl-(0,1,3)-bicyclohexane. 12.5 g (7 %) of methylisopropylbicyclohexane was obtained (after repeated fractional distillation) from 180 g of the mixture of dienes (A and B):

B. p. 150.5-150.6° (730 mm), n_D^{20} 1.4433, d_4^{20} 0.8176, MR_D 44.85. $C_{10}H_{18}$. Calculated: 44.68.

Found %: C 86.68, 86.96; H 13.16, 13.28. $C_{10}H_{18}$. Calculated %: C 86.87; H 13.13.

It was not possible to isolate the secondarily formed monocyclic hydrocarbons from the high-boiling fractions.

Raman spectra of the synthesized homologs of (0,1,3)-bicyclohexane were determined on an ISP-51 spectrograph with a slit width of 0.04 mm.

The excitation of the spectra was produced by a mercury line of 4358 A. The intensity was measured visually on a conventional scale in which the intensity frequency of 1440-1450 cm^{-1} was taken as 10 conventional units. Table 3 gives the lines of maximum intensity of the spectra of these hydrocarbons.

TABLE 3

Raman Spectra of 1-Methyl-3-Alkyl-(0,1,3)-Bicyclohexanes

Alkyl			
C_2H_5	C_3H_7	C_4H_9	Iso-C_3H_7
291 (2.5), 357 (2) 602 (2)	257 (2)	340 (2 dif), 547 (2.5)	**282** (6.5), **333** (4) **512** (3.5), 600 (2)
670 (6), **702** (5)	**671** (5), **735** (3.5)	**675** (9), **734** (4)	**664** (12), **702** (16)
799 (2.5), 873 (2)	796 (1.6 b), 876 (2)	800 (1.5)	800 (2), **853** (3.5)
893 (5), 918 (2) 930(1.8)	**897**(3.5 b) 930 (2.5)	**887** (5), 930 (1.5)	**897** (8), 934 (2)
1014 (3), 1085(1.8)	1010 (3), 1040 (2.5 b)	1012 (4.5), 1057 (1.8 dif) 1086 (1.5)	1010 (1.8 b) 1075 (2)
1106 (1.8), 1170 (3.5)	1103 (1.2, b) 1167 (1.5)	1117 (1.5), 1167 (2)	1117 (3), 1170 (2.5)
1238 (2), 1272 (3)	1270 (1.5), 1296 (1.5)	1270 (2), 1300 (2)	1270 (3)
1382 (3), 1440 (10)	1450 (10)	1387 (2), 1440 (10)	1443 (10,bg)

As may be seen from the data in Table 3 the Raman spectra of all the above-mentioned hydrocarbons have frequencies in the 670-730 cm^{-1} region (chracteristic of a quaternary carbon atom) and in the 800-890 cm^{-1} region (characteristic of three-membered and five-membered rings) which confirms their structure.

SUMMARY

Synthesis was achieved of bicyclic "bridge" hydrocarbons which had not previously been described, namely homologs of (0,1,3)-bicyclohexane with two quaternary carbon atoms in the ring, connected by a "bridge": 1-methyl-3-ethyl-, 1-methyl-3-propyl-, 1-methyl-3-butyl- and 1-methyl-3-isopropyl-(0,1,3)-bicyclohexane.

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SYNTHESIS OF HYDROCARBONS

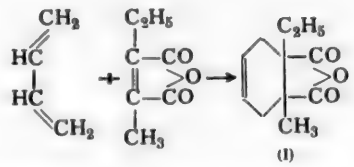
60. ETHYLBENZENE HOMOLOGS FROM ADDUCTS OF ALKADIENES WITH METHYLETHYLMALEIC ANHYDRINE

V. R. Skvarchenko, R. Ya. Levina and M. G. Kuzmin

In previous reports we described a method of preparing aromatic hydrocarbons by the reaction between phosphorus pentoxide and tetrahydrophthalic anhydrides – the reaction products of maleic [1, 2], methylmaleic [2, 3] or dimethylmaleic [2-4] anhydrides and conjugated diene hydrocarbons. From this reaction we obtained isomeric di-, tri- and tetramethylbenzenes as well as octatriene cyclopentanoindan and their homologs.

In the present work we aromatized the adducts of alkadienes with another homolog of maleic anhydride – methylethylmaleic anhydride – in order to prepare ethylbenzene homologs.

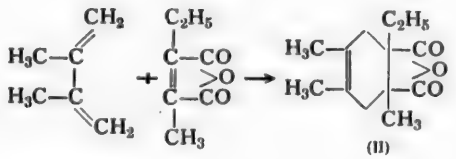
Methylethylmaleic anhydride has not been previously investigated as a dieneophil in diene synthesis. We carried out the reaction between methylethylmaleic anhydride and butadiene under drastic conditions – heating in an autoclave up to 100-120° for 20 hours, in the presence of picric acid. We obtained 1-methyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (I), which has not been described in the literature, in 78 % yield (calculated on the amount of reacted methylethylmaleic anhydride).



(I)

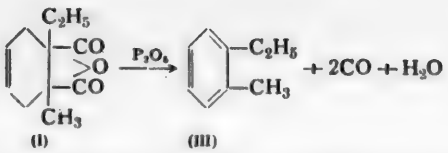
A dimer of butadiene (vinylcyclohexene) and unreacted methylethylmaleic anhydride (about 68%) were also isolated from the reaction mixture.

When heated in an autoclave for 12 hours at 140-150°, 2,3-dimethylbutadiene-1,3 and methylethylmaleic anhydride gave 1,4,5-trimethyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (II), which has not been described in the literature, in 76 % yield.



(II)

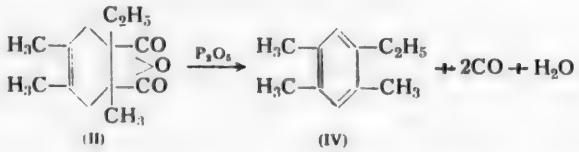
Reaction of 1-methyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (I) with phosphorus pentoxide gave o-methylethylbenzene (III) in 51% yield.



(I) (III)

o-Methylethylbenzene was oxidized to phthalic acid which was identified by the melting point of its anhydride.

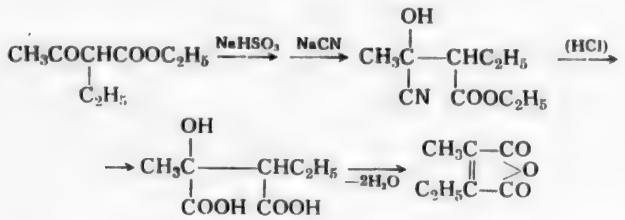
Treatment of 1,4,5-trimethyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (II) with phosphorus pentoxide gave 1,2,4-trimethyl-5-ethylbenzene (5-ethylpseudocumene) (IV), in 54 % yield.



(II) (IV)

5-Ethylpseudocumene was identified by the solidification and melting points of its sulfamide.

The starting methylethylmaleic anhydride was prepared from ethylacetoacetic ester via its cyanohydrin.



EXPERIMENTAL

Preparation of Methylethylmaleic Anhydride

Ethylacetoacetic ester (prepared by the method described for the preparation of n-butylacetoacetic ester [5]) was shaken with a saturated solution of sodium bisulfite for 12 hours. The unreacted ester was separated and shaken with a fresh portion of bisulfite (this treatment was repeated until the ester no longer dissolved). Finely ground sodium cyanide (50 g of NaCN to 200 ml of solution) was added with cooling to the bisulfite solution and after 3 hours water was added until the precipitate dissolved; the upper layer of the hydroxynitrile was separated and mixed with two volumes of concentrated hydrochloric acid and the mixture heated for 45-50 hours on a water bath (with a reflux condenser). After distilling off the water, the solid residue was dry distilled (until liquid no longer distilled off). The anhydride was separated and the aqueous layer extracted with carbon tetrachloride. The residue obtained after distilling off the solvent from the extracts was combined with the distilled anhydride and the whole distilled over phosphorus pentoxide. We isolated a fraction with b.p. 220-230°, which was distilled in vacuum to give pure methylethylmaleic anhydride (yield 30 % of theoretical, calculated on the starting acetoacetic ester):

B. p. 131° (33 mm), 123° (22 mm), 110° (10 mm); n_D^{20} 1.4720, d_4^{20} 1.1798, MR_D 33.26. $C_7H_8O_3$. Calculated: 33.52.

Literature data [6]: b.p. 122° (30 mm).

Preparation of Adducts of Diene Hydrocarbons and Methylethylmaleic Anhydride

1-Methyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride [I] was prepared by heating butadiene (40 ml) with methylethylmaleic anhydride (30 g) and picric acid (0.1 g) in an autoclave at 100-120° for 20 hours. Fractional

distillation of the reaction products in vacuum yielded vinylcyclohexene (the dimer of butadiene, b.p. 60-63° at 90 mm, n_D^{20} 1.4650; 20 g), starting methylethylmaleic anhydride (20.5 g, 68 %; b.p. 108-115° at 10 mm, n_D^{20} 1.4730) and 1-methyl-2-ethyltetrahydrophthalic anhydride (10.2 g, 78 %, calculated on the reacted methylethylmaleic anhydride):

B.p. 137° (8 mm), 143° (10 mm), n_D^{20} 1.4877, d_4^{20} 1.1391, MR_D 49.10. $C_{11}H_{14}O_3$ Calculated: 49.79.

Found %: C 68.32, 68.41; H 7.47, 7.36. $C_{11}H_{14}O_3$. Calculated %: C 68.02; H 7.27.

1,4,5-Trimethyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (II) was prepared by heating methylethylmaleic anhydride (21 g, 0.15 mole) with 2,3-dimethylbutadiene-1,3 (18 g, 0.22 mole; b.p. 69-70° at 749 mm, n_D^{20} 1.4379) in an autoclave at 140-150° for 12 hours. On distilling the reaction products in vacuum, we isolated 1,4,5-trimethyl-2-ethyl-1,2,3,6-tetrahydrophthalic anhydride (25.4 g, 76.3 %):

B. p. 141° (6.5 mm), 161° (14 mm), n_D^{20} 1.4880, d_4^{20} 1.0958, MR_D 58.44. $C_{13}H_{18}O_3$ Calculated: 59.03.

Found %: C 69.78, 69.92; H 8.29, 8.23. $C_{13}H_{18}O_3$. Calculated %: C 70.24; H 8.16.

Treatment of Tetrahydrophthalic Anhydrides with Phosphorus Pentoxide

o-Methylethylbenzene (III). 1-Methyl-2-ethyltetrahydrophthalic anhydride (I) (8.1 g, 0.04 mole) was slowly heated with phosphorus pentoxide (7 g, 0.05 mole) in a Wurtz flask with a tall outlet tube until gas was no longer evolved (about 2 hours). The reaction product was distilled off, washed with 80 % sulfuric acid, soda solution and water, dried with calcium chloride, and distilled over sodium. We obtained 2.7 g (51 %) of o-methylethylbenzene:

B. p. 165-166° (750 mm), n_D^{20} 1.5033, d_4^{20} 0.8873, MR_D 40.16. C_9H_{12}. Calculated: 40.06.

Literature data: b.p. 162° (760 mm) [7], 165.1° (760 mm)[8], $n_D^{12,2}$ 1.50656, $d_4^{12,2}$ 0.8884[7], n_D^{20} 1.50381[9].

o-Methylethylbenzene was identified by oxidation to phthalic acid (in 87 % yield), from which phthalic anhydride with m.p. 131° was obtained by sublimation. A mixture with authentic phthalic anhydride melted without depression (literature data for phthalic anhydride [10]: m.p. 130.84°).

1,2,4-Trimethyl-5-ethylbenzene (5-ethylpseudocumene) (IV). 1,4,5-Trimethyl-2-ethyltetrahydrophthalic anhydride (II) (20 g, 0.09 mole) was heated for 1.5 hours with phosphorus pentoxide (7 g, 0.05 mole), then phosphorus pentoxide (7 g, 0.05 mole) was again added; heating was continued for a further 1.5-2 hours (until gas was no longer evolved) and the reaction product was distilled off. After the usual treatment and distillation over sodium, we isolated 5-ethylpseudocumene (7.2 g, 54 %):

B. p. 208-209° (745 mm), solidification temperature -13.7 to -13.9°, n_D^{20} 1.5075, d_4^{20} 0.8888, MR_D 49.68. $C_{11}H_{16}$. Calculated 49.30.

Literature data [11]: b.p. 210° (725 mm), solidification temperature -13.58°, n_D^{20} 1.5075, d_4^{20} 0.889.

5-Ethylpseudocumene was identified by preparing 1,2,4-trimethyl-5-ethylbenzenesulfamide, which melted at 153° after recrystallization from 50 % alcohol (literature data [12]: m.p. 153°).

SUMMARY

1. Heating tetrahydrophthalic anhydrides (adducts of methylethylmaleic anhydride with conjugated dienes) with phosphorus pentoxide gave o-methylethylbenzene (51 % yield) and 1,2,4-trimethyl-5-ethylbenzene (5-ethylpseudocumene) (53 % yield).

2. Methylethylmaleic anhydride was introduced into diene synthesis for the first time. We obtained adducts of methylethylmaleic anhydride with butadiene and 2,3-dimethylbutadiene-1-3, that have not been described in the literature.

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ETHYLENE SULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH TWO HETEROCYCLIC ATOMS

II. SYNTHESIS OF 2-ALKYL-3-(CARBETHOXYPHENYL- AND 2-PHENYL-3--(CARBALKOXYPHENYL)-THIAZOLIDINES

Yu. K. Yuryev and S. V. Dyatlovitskaya

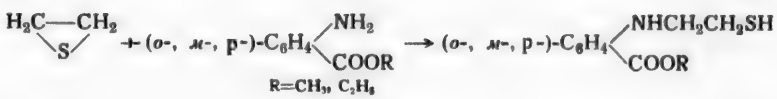
Mercaptoethylation of aliphatic amines with ethylene sulfide has been thoroughly investigated, while the analogous reaction of ethylene sulfide with amines of less basic character – aromatic ones [1-4] – has been poorly investigated.

In a previous paper by one of us [5], it was shown that the reaction of ethylene sulfide with o- and p-toluidine and o- and p-anisidine gave good yields of the corresponding N-(β-mercaptoethyl)-o- and p-toluidines and anisidines – the starting materials for the subsequent synthesis of 3-aryl- and 2,3-diarylthiazolidines.

In connection with this, it seemed interesting to investigate the reaction of ethylene sulfide with arylamines that contained an electrophilic functional group, for example carboxyl, in the nucleus. However, it was more difficult to react ethylene sulfide with aminobenzoic acids as the reaction could not be carried out in a homogeneous medium. Therefore, in this work we reacted ethylene sulfide with the esters of o-, m- and p-aminobenzoic acids.

The basicity of aminobenzoic acids and their esters is considerably lower than the basicity of aniline and its homologs: K_B^{25} for o-aminobenzoic acid and its methyl ester is equal to $1.37 \cdot 10^{-12}$ and $1.7 \cdot 10^{-12}$, respectively, for p-aminobenzoic acid and its ethyl ether – $2.42 \cdot 10^{-12}$ and $2.88 \cdot 10^{-12}$, respectively, for m-aminobenzoic acid and its methyl ester – $1.22 \cdot 10^{-11}$ and $4.36 \cdot 10^{-11}$, respectively, while K_B^{25} for aniline is $5.3 \cdot 10^{-10}$, o-toluidine - $3.3 \cdot 10^{-10}$, p-toluidine – $1.72 \cdot 10^{-9}$, m-toluidine – $6 \cdot 10^{-10}$, o-anisidine – $1.9 \cdot 10^{-10}$ (at 15°), p-anisidine – $1.47 \cdot 10^{-9}$.

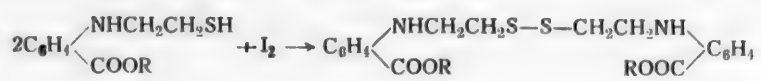
From the above data, one would expect that the esters of aromatic amino acids would react with ethylene sulfide with more difficulty than arylamines. And, indeed, more drastic conditions were needed for the preparation of the corresponding N-(β-mercaptoethyl) derivatives of aminobenzoic esters than for the preparation of N-(β-mercaptoethyl-arylamines[5]. Ethylene sulfide would react with aminobenzoic esters only on heating them to 105° in a sealed tube without solvent.



When distilled in vacuum the N-(β-mercaptoethyl)-o-, m- and p-carbalkoxyanilines, prepared by this method, decomposed vigorously. According to the literature data [2], the decomposition of aminoethylmercaptans may proceed in two directions: 1) with the formation of secondary N-alkylvinyl amines and hydrogen sulfide and 2) with the formation of the starting amines and ethylene sulfide. Due to this, analytically pure preparations could not be obtained and therefore the aminoethylmercaptans described in the literature [2] were usually characterized by preparing their crystalline derivatives.

The N-(β-mercaptoethyl)-carbalkoxyanilines, prepared in this work, were characterized by oxidizing them

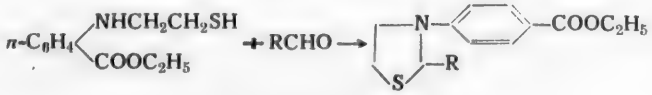
with an alcohol solution of iodine. According to the literature data [2,6], the dihydroiodides of the corresponding disulfides are formed by such an oxidation of N-alkylaminoethylmercaptans. However, we obtained only the corresponding crystalline disulfides by oxidizing N-(β-mercaptoethyl)-o-, m- and p-carbalkoxyaniline with iodine.



The formation of disulfides and not of their dihydroiodides, is explained by the lower nucleophilicity of the nitrogen atom in N-(β-mercaptoethyl) derivatives of aromatic amino acids as compared with that of N-alkylaminoethylmercaptans, caused, as mentioned above, by the lower basicity of the aminobenzoic esters that we mercaptoethylated. In the case being investigated, the small concentration of hydrogen and iodine ions formed in the reaction medium is clearly insufficient for the formation of the disulfide dihydroiodide.

In a previous paper by one of us [7], N-(β-mercaptoethyl)-arylamines were used for preparing thiazolidines, substituted in positions 2 and 3. In condensing the esters of N-(β-mercaptoethyl)-aminobenzoic acids with aldehydes, we established that the possibility of their forming thiazolidines depended to a great extent on the position of the carboxyl group in the nucleus of the mercaptoethylated aminobenzioc acid.

The condensation of N-(β-mercaptoethyl)-p-carbethoxyaniline with aldehydes proceeded smoothly to give 2-alkyl-3-(p-carbethoxyphenyl)-thiazolidines and 2-phenyl-3-(p-carbethoxyphenyl)-thiazolidine in good yields.



R = H, CH_3, C_2H_5, C_3H_7, C_6H_5.

Condensation of N-(β-mercaptoethyl)-m-carbomethoxyaniline with aldehydes gave positive results only with benzaldehyde, forming 2-phenyl-3-(m-carbomethoxyphenyl)-thiazolidine. N-(β-mercaptoethyl)-o-carbomethoxyaniline did not form a thiazolidine even with benzaldehyde. This behavior of isomeric N-(β-mercaptoethyl)--carbalkoxyanilines when condensed with aldehydes fully agrees with the behavior of N-(β-hydroxyethyl)-o- and p-toluidines in an analogous reaction [8]: N-(β-hydroxyethyl)-o-toluidine reacted solely with benzaldehyde and the corresponding oxazolidine was obtained only in low yield.

EXPERIMENTAL

Preparation of N-(β-mercaptoethyl)-o-, m- and p-carbalkoxyanilines

N-(β-Mercaptoethyl)-p-carbethoxyaniline. A mixture of 6 g (0.1 mole) of ethylene sulfide (b.p. 55.5-56°) and 33 g (0.2 mole) of ethyl p-aminobenzoate was heated for 7 hours in a sealed tube at 105°. On distilling the reaction products in vacuum in a stream of nitrogen, we isolated two fractions: 1st, b.p. 146-148° (3 mm), 20.3 g; 2nd, b.p. 184-187° (3 mm), 14.2 g.

The 1st fraction was unchanged ethyl p-aminobenzoate (m.p. 90°); the 2nd fraction was N-(β-mercaptoethyl)--p-carbethoxyaniline: m.p. 58-58.5° (from 60% alcohol). The yield was 63%, calculated on the ethylene sulfide and 82% calculated on the p-aminobenzoic ester reacting.

Found %: C 59.06, 59.04; H 6.88, 6.79. $C_{11}H_{15}O_2NS$. Calculated %: C 58.64; H 6.71.

Bis-N-(p-carbethoxyphenyl)-2-aminoethyl disulfide. A 0.1 N alcohol solution of iodine was added to a solution of 0.002 mole of N-(β-mercaptoethyl)-p-carbethoxyaniline in 5 ml of anhydrous alcohol until it was no longer decolorized.

The white precipitate was filtered off, washed with alcohol and recrystallized from alcohol; m.p. 128.5°. The yield was quantitative.

Found %: C 59.02, 59.02; H 6.42, 6.37; N 6.27, 6.41; S 14.83, 14.85. $C_{22}H_{28}O_4N_2S_2$. Calculated %: C 58.97; H 6.30; N 6.25; S 14.31.

N-(β-Mercaptoethyl)-m-carbomethoxyaniline. A mixture of 6 g (0.1 mole) of ethylene sulfide and 30.2 g (0.2 mole) of methyl m-aminobenzoate was heated for 5 hours in a sealed tube at 105°. On distilling the reaction products in vacuum in the presence of a small amount of hydroquinone in a stream of nitrogen, we isolated two fractions: 1st b.p. 130-133° (4 mm), 20.1 g; 2nd b.p. 187-188.5° (4 mm) 8.9 g.

The 1st fraction was unchanged methyl m-aminobenzoate. The 2nd fraction was N-(β-mercaptoethyl)-m--carbomethoxyaniline (a heavy yellow oil), which had the following constants after several distillations: b.p. 181.5-182.5° (3 mm), n_D^{20} 1.5936, d_4^{20} 1.1911. The yield was 42%, calculated on the ethylene sulfide and 62%, calculated on the methyl m-aminobenzoate reacting.

Bis-N-(m-carbomethoxyphenyl)-2-aminoethyl disulfide was prepared as described above; m.p. 89° (from alcohol).

Found %: C 57.32; 57.30; H 5.93, 5.95; N 6.50, 6.50; S 14.98, 14.97. $C_{20}H_{24}O_4N_2S_2$. Calculated %: C 57.12; H 5.75; N 6.66; S 15.25.

N-(β-Mercaptoethyl)-o-carbomethoxyaniline. A mixture of 7.2 g (0.12 mole) of ethylene sulfide and 37.1 g (0.243 mole) of methyl anthranilate was heated for 10 hours in a sealed tube at 105°. On distilling the reaction products in vacuum in a stream of nitrogen, we isolated two fractions: 1st b.p. 95-97° (2 mm), 25.4 g; 2nd b.p. 149-151° (2 mm), 15.6 g.

The 1st fraction was unchanged methyl anthranilate. The 2nd fraction was N-(β-mercaptoethyl)-o-carbomethoxyaniline, which had the following constants after a second distillation: b.p. 150.5-151° (2 mm), n_D^{20} 1.6019, d_4^{20} 1.1822.

The yield was 62%, calculated on the ethylene sulfide, and 95%, calculated on the methyl anthranilate reacting.

Bis-N-(o-carbomethoxyphenyl)-2-aminoethyl disulfide was prepared as described above; m.p. 80°.

Found %: C 57.13, 57.15; H 5.92, 5.82; N 6.72, 6.76; S 15.49, 15.08. $C_{20}H_{24}O_4N_2S_2$. Calculated %: C 57.12; H 5.75; N 6.66; S 15.25.

Preparation of 3-(Carbalkoxyphenyl)-Thiazolidines

3-(p-Carbethoxyphenyl)-thiazolidine. A mixture of 1.1 g (0.005 mole) of N-(β-mercaptoethyl)-p-carbethoxyaniline (dissolved in 3 ml of alcohol) and 5 ml (0.05 mole) of 33% formalin was vigorously shaken for 30 minutes. The white crystals of 3-(p-carbethoxyphenyl)-thiazolidine precipitated were filtered off, washed with water, dried and recrystallized from 70% alcohol; m.p. 92.5°. They dissolved in alcohol, ether and benzene. The yield was 1.1 g (95%).

Found %: C 60.72, 60.75; H 6.54; 6.61; N 6.27, 6.07; S 13.81, 13.63. $C_{12}H_{15}O_2NS$. Calculated %: C 60.73; H 6.37; N 5.93; S 13.51.

2-Methyl-3-(p-carbethoxyphenyl)-thiazolidine. 1.1 g (0.005 mole) of N-(β-mercaptoethyl)-p-carbethoxyaniline in 3 ml of alcohol was mixed with 2.2 g (0.05 mole) of acetaldehyde. The reaction occurred with the evolution of heat. After cooling, 0.1 g of sodium carbonate (0.001 mole) in 2 ml of water was added.

The white crystals of 2-methyl-3-(p-carbethoxyphenyl)-thiazolidine precipitated were filtered off, washed with water and cold alcohol and recrystallized from alcohol; m.p. 61-61.5°. They were soluble in benzine, benzene, ether, acetone, ethyl acetate, pyridine and dichloroethane. The yield was 0.96 g (80%).

Found %: C 62.73, 62.49; H 7.16, 6.95; N 5.82, 5.74; S 12.95, 12.94. $C_{13}H_{17}O_2NS$. Calculated %: C 62.12; H 6.82; N 5.57; S 12.76.

2-Ethyl-3-(p-carbethoxyphenyl)-thiazolidine. 1.1 g (0.005 mole) of N-(β-mercaptoethyl)-p-carbethoxyaniline in 3 ml of alcohol was mixed with 2.9 g (0.05 mole) of propionaldehyde. The reaction occurred with the evolution of heat. After 2 hours standing at room temperature (the reaction for a sulfhydryl group was negative), 5 ml of water was added. The oil precipitated was separated from the aqueous layer and traces of aldehyde were removed by distillation in vacuum.

The hydrochloride, obtained by treating an ether solution of the thiazolidine with dry hydrogen chloride,

melted (after recrystallization from alcohol) at 143° (with decomp).

Found %: C 55.38, 55.17; H 6.76, 6.72. $C_{14}H_{20}O_2NSCl$. Calculated %: C 55.71; H 6.68.

2-Propyl-3-(p-carbethoxyphenyl)-thiazolidine was prepared as described above from 1.1 g (0.005 mole) of N-(β-mercaptoethyl)-p-carbethoxyaniline and 3.6 g (0.05 mole) of butyraldehyde and appeared as a light yellow oil. The hydrochloride, prepared as described above, melted (after recrystallization from alcohol) at 144° (with decomp.).

Found %: C 56.94, 56.81; H 7.05, 7.11; N 4.76, 4.79. $C_{15}H_{22}O_2NSCl$. Calculated %: C 57.03; H7.02; N 4.44.

2-Phenyl-3-(p-carbethoxyphenyl)-thiazolidine. 1.1 g (0.005 mole) of N-(β-mercaptoethyl)-p-carbethoxyaniline in 3 ml of alcohol was mixed with 2.65 g (0.025 mole) of benzaldehyde and after 18 hours standing, 3 ml of water was added. The oil precipitated quickly crystallized. The crystals were separated off, washed with water and cold alcohol and recrystallized from alcohol; m.p. 123.5°. The yield was 1.03 g (67%).

Found %: C 68.65, 68.73; H 6.23, 6.28; N 4.84, 4.95; S 9.99, 10.05. $C_{18}H_{19}O_2NS$. Calculated %: C 68.98; H 6.11; N 4.47; S 10.23.

2-Phenyl-3-(m-carbomethoxyphenyl)-thiazolidine. 2.65 g (0.025 mole) of benzaldehyde was added to 1.05 g (0.005 mole) of N-(β-mercaptoethyl)-m-carbomethoxyaniline in 3 ml of alcohol; after standing for 20 days, the excess benzaldehyde was distilled off in vacuum. The residue crystallized; the crystals were washed with cold alcohol and recrystallized from alcohol; m.p. 76-77°. The yield was 1.05 g (70%).

Found %: C 68.08, 68.04; H 5.88, 5.94; N 4.65, 4.75; S 10.85, 10.66. $C_{17}H_{17}O_2NS$. Calculated %: C 68.20; H 5.72; N 4.68; S 10.69.

SUMMARY

1. The reaction of ethylene sulfide with aminobenzoic esters gave N-(β-mercaptoethyl)-p-carbethoxyaniline, N-(β-mercaptoethyl)-m-carbomethoxyaniline and N-(β-mercaptoethyl)-o-carbomethoxyaniline, which have not been described in the literature.

2. The corresponding disulfides were formed by treating N-(β-mercaptoethyl)-carbalkoxyanilines with a diluted alcohol solution of iodine.

3. Condensation of N-(β-mercaptoethyl)-p-carbethoxyaniline and N-(β-mercaptoethyl)-m-carbomethoxyaniline with aldehydes gave 3-(p-carbethoxyphenyl)-, 2-methyl-3-(p-carbethoxyphenyl)-, 2-ethyl-3-(p-carbethoxyphenyl)-, 2-propyl-3-(p-carbethoxyphenyl)-, 2-phenyl-3-(p-carbethoxyphenyl)- and 2-phenyl-3-(m-carbomethoxyphenyl)-thiazolidines, which have not been described in the literature.

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SYNTHESIS OF SOME 3,4-DIKETONES OF THE FURANIDINE SERIES

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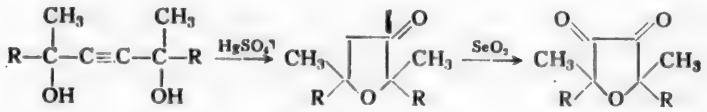
In previous papers two of us [1,2] showed that the most convenient method of synthesizing diketones of the furanidine series, containing tertiary carbon atoms in the 2 and 5 positions and carbonyl groups in the 3 and 4 positions, was by the oxidation of appropriate monoketones with selenium dioxide. The 3,4-diketones of the furanidine series formed were extremely reactive compounds; they may be used sucessfully for the synthesis of condensed heterocyclic systems, containing a furanidine and an imidazole, triazine, dihydropyrazine or quinoxaline ring [1,3].

In the present work, we preformed selenium dioxide oxidations on the following ketones of the furanidone-3 series which have not been described previously: 2,5-dimethyl-2,5-dipropylfuranidone-3, 2,5-dimethyl-2,5-diisobutylfuranidone-3 and 2,5-dimethyl-2,5-diphenylfuranidone-3. These ketones were prepared by the simultaneous hydration and dehydration of appropriate acetylene γ-glycols in the presence of mercuric sulfate. It should be noted that we did not succeed in obtaining derivatives of these ketones – 2,4-dinitrophenylhydrazones, semicarbazones, and oximes, which, apparently, was due to steric hindrance.

The oxidation of these ketones with selenium dioxide in boiling dioxan resulted in the formation of the corresponding 3,4-diketones of the furanidine series in good yields (70-90%).



R = n-C_3H_7, iso-C_4H_9, C_6H_5

2,5-Dimethyl-2,5-dipropylfuranidinedione-3,4, 2,5-dimethyl-2,5-diisobutylfuranidinedione-3,4 and 2,5-dimethyl-2,5-diphenylfuranidinedione-3,4, prepared in this work were bright crimson liquids; their absorption spectra in the visible and in the ultraviolet regions are similiar to the absorption spectra of other 3,4-diketones of the furanidine series, which we investigated previously [4]. On reacting with o-phenylendiamine they readily gave the corresponding quinoxalines in good yields.

EXPERIMENTAL

Preparation of Homologs of Furanidone-3

2,5-Dimethyl-2,5-dipropylfuranidone-3. A mixture of 31 g of 4,7-dimethyldecine-5-diol-4,7 (m.p. 50-53°) [5], 9.5 g of mercuric sulfate and 150 ml of water was boiled for 2 hours in a 300 ml round-bottomed flask, fitted with a stirrer and a reflux condenser. Then a further 9.5 g of mercuric sulfate was added and the solution boiled for another 12 hours. After cooling, the reaction mixture was extracted several times with ether. After distilling off the ether from the ether extracts, which had been dried with anhydrous sodium sulfate, the residue was twice distilled in vacuum. We obtained 23 g (74%) of 2,5-dimethyl-2,5-dipropylfuranidone-3.

B. p. 77.5-78.5° (2 mm), n_D^{20} 1.4435, d_4^{20} 0.9176, MR_D 57.26; Calc. 57.07.

Calculated %: C 72.86, 72.96; H 11.21, 11.23. $C_{12}H_{22}O_2$. Calculated %: C 72.73; H 11.11.

2,5-Dimethyl-2,5-diisobutylfuranidone-3. This was prepared as described above form 22 g of 2,4,7,9-tetra-

methyldecine-5-diol-4,7 (m.p. 55-57.5°) [6] and 12 g of mercuric sulfate. The yield was 13.3 g (60%).

B. p. 107-107.5° (7 mm), n_D^{20} 1.4447, d_4^{20} 0.9034, MR_D 66.68; Calc. 66.37.

Found %: C 74.47, 74.41; H 11.64, 11.58. $C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.48.

2,5-Dimethyl-2,5-diphenylfuranidone-3. A mixture of 32 g of 2,5-diphenylhexine-3-diol-2,5*, 7 g of mercuric sulfate and 150 ml of water was boiled for 2 hours in a 300 ml round-bottomed flask fitted with a stirrer and a reflux condenser. Then a further 7 g of mercuric sulfate was added and the solution boiled for another 13 hours. On cooling, the reaction mixture was extracted with ether and the precipitate separated by centrifuging. The ether extracts were saturated with hydrogen sulfide until all the mercuric sulfide had precipitated. The ether solution was filtered, washed with soda and water and dried with anhydrous sodium sulfate. After distilling off the ether, the residue was distilled at 170-174° (6 mm) and crystallized. We obtained 8 g (25%) of 2,5-dimethyl-2,5--diphenylfuranidone-3 with m.p. 104° (from alcohol).

Found %: C 81.12, 81.17; H 7.04, 7.20. $C_{18}H_{18}O_2$. Calculated %: C 81.20; H 6.76.

Preparation of Homologs of Furanidinedione-3,4

a) 2,5-Dimethyl-2,5-dipropylfuranidinedione-3,4. A solution of 35 g (0.3 mole) of selenium dioxide in 250 ml of moist dioxan, in a round-bottomed flask (500 ml) fitted with a stirrer, a dropping funnel and a reflux condenser, was heated to boiling and a solution of 37 g (0.18 mole) of 2,5-dimethyl-2,5-dipropylfuranidone-3 in 100 ml of dioxan was added dropwise over a period of 30-40 minutes. The reaction mixture was boiled and stirred for 16 hours. The precipitated selenium was filtered off and the dioxan distilled off from the filtrate. The residue was dissolved in ether, filtered to remove the selenium which again precipitated and dried with anhydrous sodium sulfate. After distilling off the ether, the residue was twice distilled in vacuum. We obtained 36.8 g (92%) of 2,5-dimethyl-2,5-dipropylfuranidinedione-3,4, which was a bright crimson liquid.

B. p. 92-94° (13 mm), n_D^{20} 1.4472, d_4^{20} 0.9825, MR_D 57.75; Calc. 57.08.

Found %: C 67.92, 67.71; H 9.64, 9.53. $C_{12}H_{20}O_3$. Calculated %: C 67.92; H 9.43.

2,4-Dimethyl-2,4-dipropylfuranidino-(3,4)-quinoxaline. 2.2 g of o-phenylenediamine was added to 6 g of 2,5-dimethyl-2,5-dipropylfuranidinedione-3,4. The reaction was accompanied by a change in color from dark red to yellow. The mixture was heated for several minutes in a flask with a reflux condenser; on cooling, the reaction product was dissolved in ether and dried with baked potash. After distilling off the ether, the residue was twice distilled in vacuum. We obtained 4.8 g (60%) of 2,4-dimethyl-2,4-dipropylfuranidino-(3,4)-quinoxaline.

B. p. 162-164° (4 mm), n_D^{20} 1.5335, d_4^{20} 1.0352, MR_D 85.39. $C_{18}H_{24}ON_2F_3$. Calculated 84.40.

Found %: N 9.91, 10.01. $C_{18}H_{24}ON_2$. Calculated %: N 9.85.

b) 2,5-Dimethyl-2,5-diisobutylfuranidinedione-3,4. This was prepared as described above from 15 g (0.066 mole) of 2,5-dimethyl-2,5-diisobutylfuranidone-3 and 11.1 g (0.097 mole) of selenium dioxide in 100 ml of moist dioxan. The yield was 11 g (69%). The 2,5-dimethyl-2,5-diisobutylfuranidinedione-3,4 was a bright crimson liquid.

B. p. 102-103.5° (5 mm), n_D^{20} 1.4491, d_4^{20} 0.9593, MR_D 67.2; Calc. 66.30.

Found %: C 70.08, 70.10; H 10.23, 10.32. $C_{14}H_{24}O_3$. Calculated %: C 69.96; H 10.06.

2,4-Dimethyl-2,4-diisobutylfuranidino-(3,4)-quinoxaline was prepared by the method described above from 4.8 g (0.015 mole) of 2,5-dimethyl-2,5-diisobutylfuranidinedione-3,4 and 2.16 g (0.019 mole) of o-phenylenediamine. The yield was 4 g (64%).

B. p. 172-174° (12 mm), n_D^{20} 1.5443, d_4^{20} 1.0112.

Found %: N 8.72, 8.93. $C_{20}H_{28}ON_2$. Calculated %: N 8.94.

* 2,5-Diphenylhexine-3-diol-2,5 (like the other acetylene diols, used in the present work) was prepared by Iotsich's method [5] from acetophenone and acetylenedimagnesium bromide; m.p. 163-164° (high melting form) and 122--125° (low melting form) [7].

c) 2,5-Dimethyl-2,5-diphenylfuranidinedione-3,4. This was prepared by the method described above from 20 g (0.075 mole) of 2,5-dimethyl-2,5-diphenylfuranidone-3 and 12.5 g (0.11 mole) of selenium dioxide in 150 ml of moist dioxan . The yield was 16.5 g (78 %). The 2,5-dimethyl-2,5-diphenylfuranidinedione-3,4 was a thick, bright crimson oil, which did not crystallize on long standing and came over in the range 175-190°.

Diphenylfuranidino-(3,4)-quinoxaline. 0.2 g (0.0018 mole) of o-phenylenediamine was added to 0.5 g (0.0018 mole) of 2,5-dimethyl-2,5-diphenylfuranidinedione-3,4; during the mixing heat was evolved and the color changed from bright crimson to yellow. The reaction mixture set on cooling and was recrystallized from alcohol. We obtained 0.3 g (50 %) of 2,4-dimethyl-2,4-diphenylfuranidino-(3,4)-quinoxaline with m.p. 141-142°.

Found %: N 7.94, 8.14. $C_{24}H_{20}ON_2$. Calculated %: N 7.94.

SUMMARY

Using the method we described for oxidizing the ketones of the furanidone-3 series with selenium dioxide, we obtained in good yields (70-90 %) three new examples of diketones of the furnidinedione-3,4 series: 2,5-dimethyl-2,5-dipropylfuranidinedione-3,4; 2,5-dimethyl-2,5-diisobutylfuranidinedione-3,4 and 2,5-dimethyl-2,5--diphenylfuranidinedione-3,4.

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PREPARATION OF HYDROAROMATIC HYDROCARBONS BY PYROLYZING ACETATES OF SECONDARY ALCOHOLS PREPARED FROM PRODUCTS OF DIENE SYNTHESIS

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Of the hydroaromatic hydrocarbon class with the general formula C_nH_{2n-4}, only various methadienes and vinylcyclohexene hydrocarbons – dimers of 1,3-diene hydrocarbons or formed by the dehydration of readily available tertiary alkenylcyclohexanols – have been well investigated.

In previous articles, we established the possibility of synthesizing hydroaromatic hydrocarbons with the above formula from hydroaromatic ketones or esters, which were the condensation products of 1,3-diene hydrocarbons with α,β-unsaturated ketones or esters [1-3]. These hydroaromatic ketones or esters were treated with organomagnesium compounds to convert them to tertiary alcohols, which were then dehydrated with acetic anhydride. Other authors also prepared hydroaromatic alcohols by this method [4-7].

Secondary alcohols were also prepared from α,β-unsaturated aldehydes by an analogous scheme, but previously they could not be converted into hydrocarbons by the same method [1]. In this article we describe further experiments in this direction.

We investigated alcohols formed by methylmagnesium iodide and ethylmagnesium iodide treatment of hydroaromatic aldehydes – condensation products of divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene and cyclohexadiene with acrolein and partly with crotonaldehyde.

Many authors [8] have investigated the condensation of diene hydrocarbons with the simplest unsaturated aldehydes. Nevertheless, the condensation order in the case of unsymmetric dienes (piperylene and isoprene) required additional investigation and consideration.

B. A. Arbuzov, Z. Zinoveva and I. Fink [4] were the first to react piperylene with acrolein but without proof, the authors proposed the formula 3-methyl-Δ^4-tetrahydrobenzaldehyde for the reaction product. Later on, one of us showed that the main substance here was another isomer, namely 2-methyl-Δ^3-tetrahydrobenzaldehyde [9]. B. A. Arbuzov and E. G. Kataev then confirmed the latter formula in a new paper devoted to the order of diene synthesis [10].

Previously, we also established the structure of the main condensation product of isoprene with acrolein [1]. Crystalline 4-methyl-Δ^3-tetrahydrobenzoic acid was obtained by oxidizing the substance. Consequently, the starting aldehyde had the aldehyde and methyl groups para to each other.

In this work we investigated more thoroughly the condensation order of piperylene and isoprene with acrolein; in it, we showed that both in the case of piperylene and in the case of isoprene a mixture of the two possible isomers was formed, containing approximately 85% of the main isomer. Thus, all the products, obtained from these two hydrocarbons, were mixtures with one isomer predominating (ortho- in the case of piperylene and para- in the case of isoprene).

The preparation of the secondary hydroaromatic alcohols used in this work from aldehydes is described in several articles [1,4,7]. We prepared a series of alcohols of this class, some of which have and some of which have not been described in the literature. Their formulas and constants are given in Table 1 and these data show that the elongation of a side chain by one methyl group causes a greater increase in the homolog's boiling point than

the introduction of this group into the nucleus. In the latter case, the para-isomers boil at a higher point than the ortho-isomers. The refractive indices of all homologs and isomers and the specific gravities of the isomers are similiar to each other. The refractive indices and specific gravities decrease slightly with the elongation of the side chain. Bicyclic alcohols have lower boiling points and considerably higher specific gravities and refractive indices than the monocyclic ones.

The most important operation in this synthesis of hydroaromatic hydrocarbons is the dehydration of the alcohols prepared by the above method. The dehydration conditions had to be selected in such a way that only one of the two possible isomeric hydrocarbons would be formed.

A number of authors have shown that the most sucessful method of dehydration for this purpose is the pyrolysis of acetates [11-13] and, therefore, we used this particular method.

The synthesis of acetates from alcohols did not present any difficulties. The constants of the acetates we prepared are given in Table 2. The data in the table show that acetates boil at approximately 8° higher, have somewhat greater specific gravities and considerably smaller refractive indices than the starting alcohols.

We rechecked the accuracy of the rule established earlier that dehydration proceeds in one direction during acetate pyrolysis, using as an example the pyrolysis of the acetate of methyl-(cyclohexen-3-yl)-carbinol. During its pyrolysis we observed only the formation of vinylcyclohexene-3, which had constants completely identical to the usual divinyl dimer.

Thus, all the hydrocarbons, obtained from symmetrical dienes, may be confidently assigned the formulas of alkylated vinylcyclohexenes, given in Table 3. Hydrocarbons, prepared from piperylene and isoprene, were mixtures of two isomers with a considerable predominance of those whose formulas are given in Table 3.

To establish their structures two hydrocarbons were dehydrogenated on platinum and the dehydrogenation products were oxidized with dilute nitric acid under pressure in sealed tubes. • The hydrocarbon, prepared from methyl-(methylcyclohexen-3-yl)-carbinol, synthesized from piperylene, gave phthalic and a little (14.5%) isophthalic acid. The hydrocarbon from methyl-(methylcyclohexen-3-yl)-carbinol, prepared from isoprene, gave terephthalic and a little (14%) isophthalic acid. It was thus shown that in condensing piperylene and isoprene with acrolein, the possible isomers of the hydroaromatic aldehydes are formed in a ratio of 6:1.

The pyrolysis of acetates gave the expected hydrocarbons in all but one case. On pyrolyzing the acetate of methyl-(2,5-endomethylenecyclohexen-3-yl)-carbinol, the ring was opened and the reaction products were butenyl acetates. Apparently, cyclopentadiene was a second reaction product.

The constants of the hydrocarbons obtained are given in Table 3. The data in this table show that in the case of hydrocarbons, as in the case of alcohols, the introduction of a methyl group into the side chain increased the boiling point more than the introduction of this group into the nucleus. Isomers with radicals in the para-position in the nucleus have a higher boiling point than ortho-isomers. It should also be noted that the boiling points of the hydrocarbons were not sharp in certain cases (2-3°), possibly due to the formation of a mixture of geometric isomers.

The hydroaromatic hydrocarbons of the type investigated were readily dehydrogenated on platinized charcoal; therefore, on passing the acetates of the appropriate alcohols over platinized charcoal, the elimination of acetic acid and dehydrogenation of the hydrocarbon occurs simultaneously and, as a result, aromatic hydrocarbons are the immediate reaction products. We observed this process in two acetates – those of methyl-(2,5-dimethylcyclohexen-3-yl)-carbinol and ethyl-(2,5-dimethylcyclohexen-3-yl)-carbinol.

In conclusion, we noted that many of the hydroaromatic hydrocarbons that we prepared are of interest as they are the dimers or mixed "dimers" of diene hydrocarbons [16]. Thus, for example, hydrocarbons (II), (VII) and (IX) are mixed "dimers" of divinyl and piperylene, hydrocarbon (XI) – of divinyl and isoprene, hydrocarbon (XV) – of divinyl and diisopropenyl, hydrocarbon (XII) – of isoprene and piperylene. Hydrocarbon (X) is the normal piperylene dimer.

• Since 1953 we have used this method of oxidizing aromatic hydrocarbons under pressure to determine the structure of hydroaromatic hydrocarbons [15]. I. N. Nazarov, A. I. Kuznetsova and N. V. Kuznetsov reported it in 1955 [14].

EXPERIMENTAL •

All the hydroaromatic aldehydes used in this investigation have been described in the literature [8]. The constants of the materials we prepared were the same as those found in the literature; therefore, we do not give them in this article.

The method of preparing the secondary alcohols was described in one of the previous reports [1]. The constants, analytical data and yields (for the substances prepared again) are given in Table 1••.

Acetylation was performed with acetic anhydride in the presence of a drop of sulfuric acid. The constants, analytical data and yields for the acetates are given in Table 2.

The acetates were pyrolized at 400-450° in a silica tube filled with small spirals of heat resistant glass. The substances were passed through the tube at 1-2 drops a minute. Carbonization of the glass was not observed. Part of the acetate was recovered unchanged. The condensate was freed from acetic acid by washing with soda solution, dried with baked sodium sulfate and distilled in vacuum on a Widmer column. The constants, analytical data and yields for the hydrocarbons are given in Table 3.

As a result of pyrolizing the acetate of methyl-(2,5-endomethylenecyclohexen-3-yl)-carbinol, we obtained a small amount of an oil (apparently a mixture of the acetates of methylvinylcarbinol and crotonyl alcohol).

B. p. 127-129°, d_4^{20} 0.9212, n_D^{20} 1.4224, MR 31.52; Calc. 31.19.

Found %: C 63.43, 63.45; H 9.08, 9.15; CH_3CO_2 52.34. $C_4H_7OCOCH_3$. Calculated %: C 63.13; H 8.83; CH_3CO_2 51.73.

On bromination, 0.0598 and 0.0483 g of substance consumed 0.0779 and 0.0625 g of bromine, which corresponds to a 92-93 % content of the unsaturated acetate with the formula shown above.

For the acetate of methylvinylcarbinol, the following constants are given in the literature [17]: b.p. 111-112°, d_4^{20} 0.9024, n_D^{20} 1.4039. For the acetate of crotonyl alcohol [17]: b.p. 132.5-133.5°, d_4^{20} 0.9192, n_D^{20} 1.4192.

The hydrocarbon (IX), prepared from the condensation product of piperylene and acrolein (6.5 g), was dehydrogenated on platinized charcoal, prepared by the usual method [18]. We obtained a mixture of o- and p-methylethylbenzenes (3.6 g) with a considerable preponderance of the former.

B. p. 164-165°, d_4^{20} 0.8837, n_D^{20} 1.5070.

The following constants are given in the literature [19]: o-methylethylbenzene b.p. 165.15°, d_4^{20} 0.8807, n_D^{20} 1.5046; m-methylethylbenzene b.p. 161.31, d_4^{20} 0.8645, n_D^{20} 1.4966.

2.7 g of the aromatic hydrocarbon was oxidized with dilute nitric acid (25 %) under pressure (in sealed tubes) at 150-160°. After cooling and opening the tubes, the crystalline mass was filtered off, the bulk of the nitric acid in the liquid neutralized with soda and the solution extracted with ether. Almost exclusively o-phthalic acid was found in the acid solution. The crystalline part consisted of o- and isophthalic acids. These acids were separated by fractional crystallization from water. We obtained 1.66 g of o-phthalic acid with m.p. 190-191°. Distillation of the acid in vacuum with acetic anhydride yielded phthalic anhydride with m.p. 131°. 0.28 g of isophthalic acid was isolated. The m.p. was 335°. The substance was heated on a water bath in methanol in the presence of a small amount of sulfuric acid. On cooling, crystals of dimethyl isophthalate with m.p. 66-67° precipitated.

The hydrocarbon (XI), prepared from isoprene and acrolein, was also dehydrogenated. From 6.5 g of the hydrocarbon we obtained 3.6 g of methylethylbenzene [19]. The b.p. was 160-162°, d_4^{20} 0.8594, n_D^{20} 1.4962.

On oxidation by the method described above, 2.7 g of the hydrocarbon gave 1.4 g of terephthalic acid (dimethyl ester with m.p. 140-141°) and 0.24 g of isophthalic acid (m.p. 346°; dimethyl ester with m.p. 66-67°).

On passing the acetates of hydroaromatic alcohols over platinized charcoal at 350°, we observed the formation of predominantly aromatic hydrocarbons. We prepared two hydrocarbons by this method. From the acetate

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•With the assistance of M.L. Kovner

••It is possible that the hexadiene-2,4, used both for this work and for a lot of other work, contained isomers. It was isolated from the still residues from the production of synthetic rubber.

TABLE 1

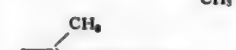
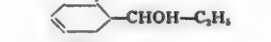
Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D		Found %			Calculated %			Yield (in %)
				Found	Calculated	C	H	OH	C	H	OH	
	93—93.5°	0.9592	1.4842	37.65	38.00 [1]							
	104—104.5	0.9503	1.4832	42.16	42.62 [1]							
	113.5—114	0.9336	1.4806	46.98	47.24	78.21	11.94	11.59	77.87	11.76	11.03	73.0
	106—107	0.9463	1.4830	46.55	47.24	77.71	12.04	11.27	77.87	11.76	11.03	63.3
	131.5—132	0.9256	1.4795	51.60	51.85	78.65	12.09	10.42	78.51	11.98	10.11	59.5
	121.5—122.5	0.9221	1.4775	51.61	51.85	78.58	12.27	10.28	78.51	11.98	10.11	50.6
	101—101.5	0.9465	1.4822	42.25	42.62	77.14	12.04	11.95	77.08	11.50	12.13	68.5
	108.5—109.5	0.9406	1.4830	46.83	47.24	77.66	11.52	10.96	77.87	11.76	11.03	58.5
	102—102.5	0.9492	1.4834	42.22	42.62 [1]							
	111.5—112	0.9406	1.4830	46.83	47.24 [1]							
	106.2	0.9421	1.4834	42.53	42.62 [1]							

TABLE 1 (Continued)

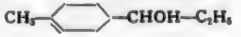
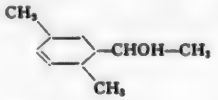
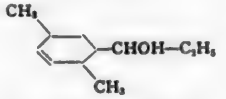
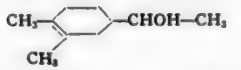
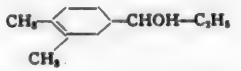
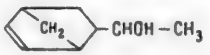
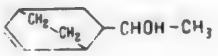
Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D		Found %			Calculated %			Yield (in %)
				Found	Calculated	C	H	OH	C	H	OH	
	116.5—117	0.9374	1.4828	46.98	47.24[1]							
	110.5—111.5	0.9349	1.4826	47.09	47.24	78.07	11.83	11.18	77.87	11.76	11.03	52.0
	118—119	0.9365	1.4851	51.51	51.85	78.58	11.77	10.47	78.51	11.98	10.11	70.7
	118—119	0.9385	1.4890	47.44	47.24	77.63	12.02	11.18	77.87	11.76	11.03	74.7
	126—127	0.9359	1.4876	51.76	51.85	78.93	11.91	10.47	78.51	11.98	10.11	68.5
	91.5—92.5	1.0012	1.4935	40.15	40.42	78.23	10.14	12.02	78.21	10.21	12.31	67.7
	109—110 (18 мм)	0.9998	1.5029	45.00	45.04[7]							

TABLE 2

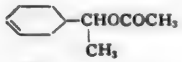
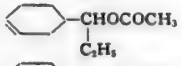
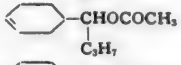
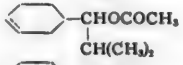
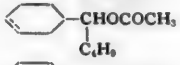
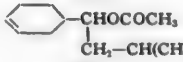
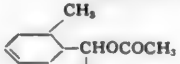
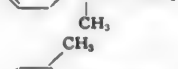
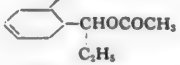
Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D		Found %		Calculated %		Yield (in %)
				Found	Calculated	C	H	C	H	
	101—101.5°	0.9777	1.4594	47.08	47.37[1]					
	113—114	0.9668	1.4608	51.71	51.98[1]					
	121—122.	0.9559	1.4609	56.33	56.60	73.40, 73.06	9.99, 10.04	73.42	10.27	84.2
	114—115	0.9610	1.4632	56.28	56.60	73.31, 73.61	10.48, 10.61	73.42	10.27	84.3
	137.5—138	0.9458	1.4610	61.01	61.22	74.30, 74.52	10.75, 10.82	74.24	10.55	76.0
	129.5—130.5	0.9445	1.4603	61.02	61.22	74.12, 74.26	10.89, 10.63	74.24	10.55	79.1
	107.5—108	0.9665	1.4612	51.76	51.98	72.50, 72.78	10.21, 9.96	72.49	9.95	88.0
	118—118.5	0.9584	1.4620	56.30	56.60	73.26, 73.76	10.55, 10.47	73.42	10.27	68.0
	108—108.5	0.9650	1.4632	52.04	51.98	72.50, 72.48	10.24, 10.08	72.49	9.95	74.0

TABLE 2 (Continued)

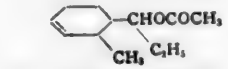
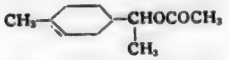
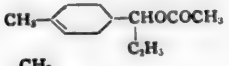
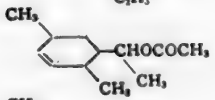
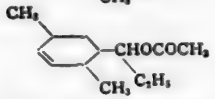
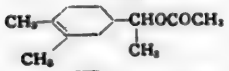
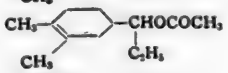
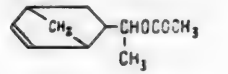
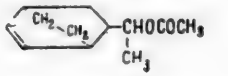
Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR_D		Found %		Calculated %		Yield (in %)
				Found	Calculated	C	H	C	H	
	118.5—119.5°	0.9569	1.4641	56.61	56.60	73.50, 73.44	10.45, 10.61	73.42	10.27	70.0
	113.5—114.5	0.9612	1.4618	52.11	51.98	72.70, 72.19	10.03, 10.05	72.49	9.95	74.4
	124.5—125.5	0.9536	1.4628	56.67	56.60	73.18, 73.19	10.35, 10.60	73.42	10.27	68.6
	119—120	0.9593	1.4658	56.65	56.60	73.51, 73.15	10.42, 10.46	73.42	10.27	73.4
	126—127	0.9525	1.4660	61.15	61.20	74.61, 74.14	10.64, 10.63	74.24	10.54	71.4
	125.5—126	0.9598	1.4681	56.86	56.60	73.49, 73.70	10.53, 10.39	73.42	10.27	67.9
	134—135	0.9524	1.4713	61.75	61.22	74.47, 74.06	10.50, 10.70	74.24	10.54	72.4
	102—103	1.0061	1.4660	49.61	49.78	73.53, 73.29	9.35, 9.23	73.30	8.94	83.9
	119—120	1.0184	1.4780	54.02	54.40	74.21, 74.09	9.64, 9.24	74.18	9.33	61.4

TABLE 3

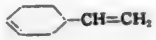
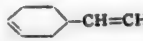
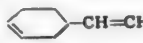
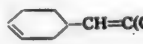
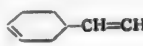
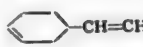
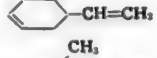
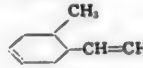
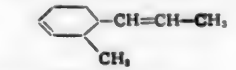
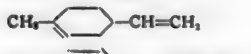
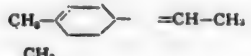
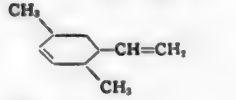
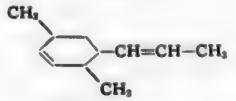
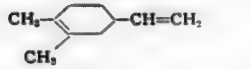
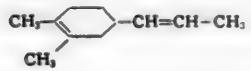
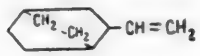
Substance		Boiling point at a given pressure (mm)	d_4^{20}	n_D^{20}	MR_D		Found %		Calculated %		Yield (in %)
					Found	Calculated	C	H	C	H	
	(I)	66.5—67.5° (100)	0.8303	1.4648	35.98	36.01					
	(II)	91.5—93 (100)	0.8392	1.4755	41.03	40.63	88.22, 88.36	11.88, 11.84	88.45	11.55	67.7
	(III)	109.5—110.5 (100)	0.8413	1.4740	45.51	45.25	87.92, 88.29	12.20, 12.08	88.16	11.84	52.5
	(IV)	106—107 (100)	0.8434	1.4760	45.56	45.25	87.89, 87.94	11.70, 11.72	88.16	11.84	42.0
	(V)	127—128 (100)	0.8403	1.4720	50.07	49.86	87.92, 88.16	12.28, 11.93	87.92	12.08	46.1
	(VI)	118—119 (100)	0.8522	1.4695	49.15	49.86	87.69, 87.89	11.92, 11.81	87.92	12.08	20.6
	(VII)	79—80 (100)	0.8293	1.4658	40.80	40.63	88.75, 88.25	11.68, 11.88	88.45	11.55	58.2
	(VIII)	100—104 (100)	0.8374	1.4718	45.54	45.25	88.00, 87.94	12.05, 11.52	88.16	11.84	43.8
	(IX)	83—85 (100)	0.8364	1.4702	40.78	40.63	88.74, 88.41	11.84, 11.69	88.45	11.55	66.5

TABLE 3 (Continued)

Substance		Boiling point at a given pressure (mm)	d_4^{20}	n_D^{20}	MR_D		Found %		Calculated %		Yield (in %)
					Found	Calculated	C	H	C	H	
	(X)	101.5—103.5° (100)	0.8399	1.4748	45.65	45.25	87.91, 88.04	12.16, 12.04	88.16	11.84	65.5
	(XI)	87—90 (100)	0.8326	1.4715	41.06	40.63	88.80, 88.68	11.78, 11.56	88.45	11.55	57.0
	(XII)	110—111 (100)	0.8412	1.4770	45.76	45.25	88.06, 88.24	12.06, 12.05	88.16	11.84	79.3
	(XIII)	68—72 (20)	0.8533	1.4778	45.17	45.25	88.11, 88.25	11.80, 11.58	88.16	11.84	45.7
	(XIV)	83.5—85 (20)	0.8695	1.4822	49.28	49.86	88.20, 88.10	12.35, 11.71	87.92	12.08	42.2
	(XV)	70.5—71.5 (20)	0.8466	1.4785	45.59	45.25	88.15, 87.97	11.60, 12.06	88.16	11.84	59.2
	(XVI)	87—87.5 (20)	0.8498	1.4820	50.41	49.86	87.76, 88.22	12.27, 12.17	87.92	12.08	64.2
	(XVII)	71—74	0.9254	1.5050	43.02	43.04	89.22, 89.50	10.85, 10.66	89.49	10.51	42.3

of methyl-(2,5-dimethylcyclohexen-3-yl)-carbinol we obtained 1,4-dimethyl-2-ethylbenzene [19]. The b.p. was 184-185°, d_4^{20} 0.8830, n_D^{20} 1.5035.

From the acetate of ethyl-(2,5-dimethylcyclohexen-3-yl)-carbinol we obtained 1,4-dimethyl-2-propylbenzene [19]. The b.p. was 205-206°, d_4^{20} 0.8705, n_D^{20} 1.4918.

Both aromatic hydrocarbons probably contained traces of the corresponding hydroaromatic hydrocarbons.

SUMMARY

1. A series of secondary hydroaromatic alcohols were prepared by reacting organomagnesium compounds with hydroaromatic aldehydes, which were the condensation products of divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene and cyclohexadiene with acrolein and partly with crotonaldehyde.

2. The acetates of these alcohols were prepared and characterized.

3. Pyrolysis of the acetates, with the exception of the acetate of methyl-(2,5-endomethylenecyclohexen--3-yl)-carbinol, gave the corresponding hydroaromatic hydrocarbons, which in structure were the dimers or mixed "dimers" of 1,3-diene hydrocarbons.

4. Pyrolysis of the acetate of methyl-(2,5-endomethylenecyclohexen-3-yl)-carbinol gave butenyl acetates in a low yield.

5. It was shown that condensation of piperylene and isoprene with acrolein gave mixtures of isomeric hydroaromatic aldehydes and the mixture consisted of about 85 % of the ortho-isomer, in the case of piperylene, and the para-isomer, in the case of isoprene.

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* Original Russian pagination. See C. B. Translation.

** In Russian.

INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

LXXVI. THE ORDER OF BROMINE ADDITION TO ALKENYL- AND ISOALKENYLACETYLENES

A. A. Petrov and Yu. I. Porfireva

In work previously published by our laboratory, it was shown that two types of close homologs of vinylacetylene ($R-C\equiv C-CH=CH_2$ and $CH_2=CR-C\equiv CH$) add bromine at the ethylene bond [1,2], i.e. the same as vinylacetylene hydrocarbons with isolated multiple bonds [3] and differently from unsubstitute vinylacetylene (1,4-addition [4,5]). In order to elucidate the reasons for this behavior, it was necessary to investigate the order of bromine addition to vinylacetylene hydrocarbons of yet another type, ($R-CH=CH-C\equiv CH$), alkenylacetylenes. In addition, the reaction of isoalkenylacetylenes with bromine needed to be investigated more thoroughly, as previously this had been done for only one example (isopropenylacetylene) [2].

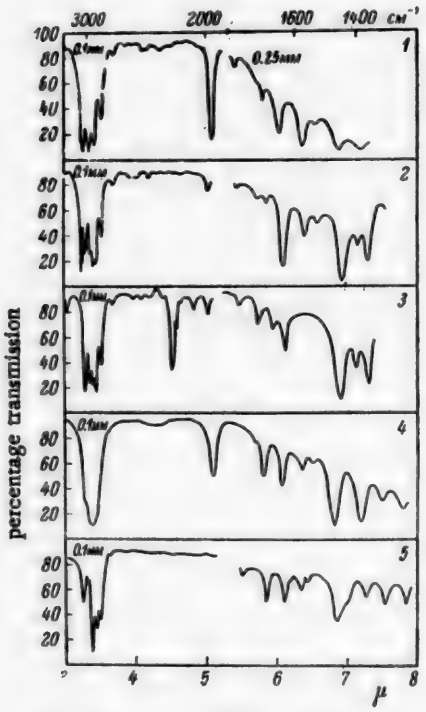

Fig. 1. Infrared transmission spactra. 1) Propenylacetylene dibromides, 2) product of their isomerization (1,2-dibromopentadiene-1,3), 3) products of their dehalogenation, 4) butenylacetylene dibromides, 5) product of their isomerization (1,2-dibromohexadiene-1,3).

This article describes the experimental results of the bromination of alkenylacetylenes – propenylacetylene (penten-3-ine-1) and butenylacetylene (hexen-3-ine-1) and isoalkenylacetylenes – β-tert-butylvinylacetylene (1',1'-dimethyl-3-ethylbuten-3-ine-1) and 3-methylpenten-3-ine-1. Some additional experiments were also devised for investigating the structure of isopropenylacetylene and vinylethylacetylene dibromides.

From bromine addition to propenyl- and butenylacetylene, one would expect the formation of the following three substances:

$$R-CHBr-\underset{(I)}{CHBr-C\equiv CH}$$

$$R-CH=CH-\underset{(II)}{CBr=CHBr}$$

$$R-CHBr-\underset{(III)}{CH=C=CHBr}$$

Experiments showed that, actually, a mixture of the allene (III) (predominantly) and 1,3-diene (II) dibromides were obtained without the third possible isomer.

The problem of the structure of the dibromides obtained was solved unequivocally by investigating their chemical properties and infrared spectra.

1. When treated with alcoholic alkali in the cold, they rapidly lost 35-40% bromine with the formation of vinylacetylene monobromides. In the residue remained the 1,3-diene dibromide (II), which was stable to treatment by alcoholic alkali and was somewhat contaminated with the products of substituting methoxyls for bromine.

2. When heated with hydrobromic acid and Cu_2Br_2 in an ether solution, they were isomerized into 1,3--diene dibromides that were stable to the action of alcoholic alkali.

3. When treated with an ammonia solution of silver oxide, they slowly formed a small precipitate which was mainly AgBr.

4. The infrared spectra of the starting dibromides had intense absorption bands at 5.09 μ, characteristic of allene compounds, as well as two frequencies in the region of 6-6.4 μ, characteristic of diene halogen derivatives [5]. We did not detect in the spectra, absorption bands corresponding to an acetylene grouping at the end of the chain (in the region of 3.03 and 4.6-4.8 μ), (Fig. 1, Curves 1 and 4).

It was thus established that bromine adds to alkenylacetylenes in the 1,4 and 1,2-positions. It is possible that 1,2-products are formed as a result of isomerization at the moment of formation of the 1,4-products.

It should be noted that 1,2-dibromides (II), formed as a result of 1,4-dibromide isomerization with HBr and Cu_2Br_2, contain almost no traces of the starting allene dibromide. Only the frequencies of 1,3-diene systems are clearly expressed in their spectra (in the region of 6-6.4 μ Fig. 1, Curves 2 and 5).

In dehalogenation of the allene dibromide (III) of propenylacetylene with alcoholic alkali, the formation of several isomeric monobromides is possible.

$$CHBr{=}C{=}CH{-}CHBr{-}CH_3 \rightarrow \begin{cases} CBr{\equiv}C{-}CH{=}CH{-}CH_3 & (IV) \\ CH{\equiv}C{-}CH{=}CBr{-}CH_3 & (V) \\ CHBr{=}C{=}CH{-}CH{=}CH_2 & (VI) \\ CHBr{=}C{=}C{=}CH{-}CH_3 & (VII) \end{cases}$$

Under analogous conditions 4-chlorobutadiene-1,2 gave vinylacetylene [6] and the 1,4-dibromide of vinylacetylene – 1-bromobuten-2-ine-1 [4]. From this data, the most probable reaction product in the case being investigated would be vinylacetylene monobromide (IV).

Actually the infrared spectrum of the monobromide, obtained from propenylacetylene dibromide showed an intense frequency, characteristic of disubstituted acetylenes* (4.52 μ) and the frequency of a double bond at 6.13 μ. The frequencies of the end acetylene group (3.03 μ) and allene system (5.09 μ) were very weakly expressed. Consequently, the isomeric monobromides (V), (VI) and (VII) were present only as traces (Fig. 1, Curve 3). One can conclude from this data that dehalogenation of the allene dibromide (II) proceeded mainly by the scheme

$$H{-}\overset{\curvearrowright}{CBr}{=}C{=}\overset{\curvearrowright}{CH}{-}\underset{\underset{Br}{|}}{CH}{-}CH_3 \xrightarrow{-HBr} CBr{\equiv}C{-}CH{=}CH{-}CH_3 \quad (IV)$$

Bromination of isopropenylacetylene gave mainly the acetylene dibromide $CH{\equiv}C{-}\underset{\underset{R}{|}}{CBr}{-}CH_2Br$. The structure of the substance was established by chemical methods. To supplement this data that had been previously published, we investigated the infrared spectra of the main fraction of isopropenylacetylene dibromides with b.p. 51-53° (10 mm) and the one with a higher b.p. of 70-80° (10 mm), as well as the ozonization rate of the main fraction.

The infrared spectrum of the main fraction (Fig. 2, Curve 1) confirmed the conclusion made earlier that the substance was mainly the acetylene dibromide. The frequencies of the end acetylene group were quite intense in this spectrum. The frequency of 5.82 μ, whose nature has not been clarified and which is usually found in spectra of acetylene compounds, was also quite intense [8]. The frequencies 6.03 and 6.22 μ found in the spectrum were due to traces of 1,3-diene dibromide. Even with a thicker layer (0.25 mm) the frequency of the allene system had a low intensity; therefore, we can consider it established that there was practically no allene dibromide in this fraction.

The fraction 70-80° (10 mm), on the contrary, judging from the infrared spectrum (Fig. 2, Curve 1 – dotted),

* Alkylhaloacetylenes absorb as disubstituted acetylenes [7].

contained a considerable amount of the allene dibromide besides the other two isomers (diene and acetylene).

Thus, the conclusions on the structure of isopropenylacetylene dibromides arrived at earlier on the basis of chemical data, were confirmed by the analysis of infrared spectra: although isopropenylacetylene adds bromine in the same order as vinylalkylacetylenes, it has greater affinity for 1,4- and 3,4-addition.

The curve of the ozonization rate of the main fraction 51-53° (10 mm) did not have any inflexions up to the absorption of 1 mole of ozone, which indicates that the substance is relatively pure (Fig. 3).*

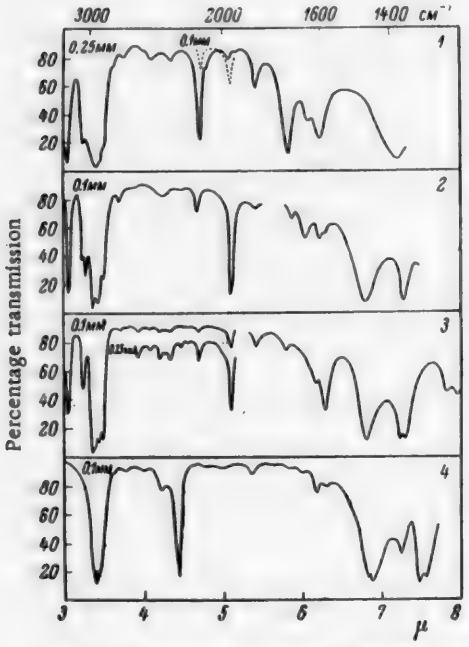

Fig. 2. Infrared transmission spectra.
1) Isopropenylacetylene dibromides,
2) 3-methylpenten-3-ine-1 dibromides,
3) tert-butylvinylacetylene dibromides,
4) vinylethylacetylene dibromides.

It was interesting to compare the experimental results of the bromination of isopropenylacetylene with the experimental results of the bromination of its homolog with a tertiary butyl radical — 1',1'-dimethyl-3-ethylbuten-3-ine-1, First of all, one would expect here lower activity of the double bond due to the absence of conjugation with the CH_3-group (absence of the Baker-Nathan effect) and, secondly, the presence of steric hindrance(screening of the double bond by the tertiary butyl radical).

The dibromide of tert-butylvinylacetylene actually obtained was mainly a 1,3-diene compound. It was found to be stable to the action of alcoholic alkali. It gave a large amount of formaldehyde when ozonized. On the infrared spectrum of this dibromide, the absorption bands characteristic of allene and especially acetylene groups were expressed more weakly than in the spectrum of the dibromide of isopropenylacetylene. On the contrary, the frequencies of 1,3--diene systems (6.17 and 6.28μ) were intense (Fig. 2, Curve 3).

Thus, our hypotheses were confirmed. The reaction, apparently, started and ended in this case to a great extent within the limits of the acetylene bond. The absence of double bond activiation by the conjugation mechanism made the triple bond a more vulnerable place for the start of the reaction. At the same time a voluminous radical hindered the formation of an allene compound.

To substantiate our conclusions on the effect of radicals on the vinylacetylene system, it was necessary to establish the order of bromine addition to hydrocarbons, in whose molecules these radicals would act in opposite directions. As an example we selected 3-methylpenten-3-ine-1 for the investigation.

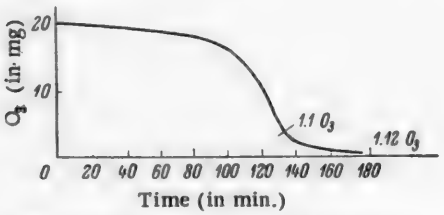

Fig. 3. Ozonization curve of isopropenylacetylene dibromide.

The addition of bromine to this hydrocarbon gave a mixture of all three possible isomeric dibromides in similiar amounts. When treated with alcoholic alkali in the cold, the dibromides of this hydrocarbon lost about 40 % of the bromine. Consequently, the mixture contained about 80 % of a mixture of acetylene and allene dibromides and about 20 % of the 1,3-diene.

The infrared spectrum of the dibromides (Fig. 2, Curve 2) had, besides the frequencies of 1,3-diene

* The authors thank N. G. Kasatkina for investigating the ozonization rate of this dibromide in this work.

dibromide, intense frequencies of allene (5.09μ) and acetylene dibromides (3.03 and 4.67μ). Judging from the spectrum, the allene dibromide predominated. Thus, the conjugation effect with the participation of the methyl group in a normal chain was found to be stronger than with the participation of a branch methyl group.

For comparison, we also plotted the spectrum of vinylethylacetylene dibromide (Fig. 2, Curve 4). There were no frequencies of allene systems here at all and the frequencies of 1,3-diene systems were very weak. The frequency of the triple bond was clearly expressed. We concluded from the chemical data as well that the substance was an acetylene dibromide [1].

In conclusion, one should note that in treating a mixture of allene and acetylene dibromides with HBr and Cu_2Br_2, the allene was isomerized much more rapidly than the acetylene dibromide. There was usually no allene dibromide in the isomerization products and, at the same time, insignificant amounts of acetylene dibromide were always found, even in the case when the reaction time was considerably increased.

In exactly the same way it was noted that allene dibromide was capable of partial isomerization to 1,3--diene dibromide when heated. In order to avoid errors in determining the direction of bromine addition, which may occur due to isomerization of the dibromides in separating by distillation, we carried out bromination experiments at -20° with small samples (0.3-0.5 g) of hydrocarbons in CCl_4 with a ratio of hydrocarbon:bromine = 1 : 1 and investigated the infrared spectra of the solutions obtained; from this we obtained data which were exactly the same qualitatively as in the investigation of the structure of distilled dibromides. The greatest change in the ratio between isomeric dibromides was found for isopropenylacetylene. The distilled mixture contained a smaller amount of allene dibromide than the starting solution of dibromides.

The experimental results described above on the order of bromineaddition to vinylacetylene hydrocarbons make it possible to draw general conclusions. It was established that the double bond in systems with isolated multiple bonds was more reactive in relation to bromine than the triple bond. Vinylacetylene hydrocarbons with isolated multiple bonds added bromine practically exclusively at the double bond. In the conjugated vinylacetylene system bromine may possibly be added at the ends of the conjugated system, apparently, with the initial attack at the triple bond and with subsequent partial isomerization of the allene into 1,3- dibromide. Such an addition order occurs to a large extent only in the case of vinylacetylene and alkenylacetylenes with normal structure. Vinylalkylacetylenes and isoalkenylacetylenes (without a radical on the starting atom at the double bond) add bromine mainly as compounds with isolated multiple bonds. Isoalkenylacetylenes were found to have an increased tendency to add at the triple bond.

These rules on the orientation of a bromine molecule, at the moment of addition, in relation to the vinylacetylene system are in accordance with the usual ideas on the theory of electronic displacement. If one supposes that radicals may induce displacement of the electron cloud in a conjugated system towards the ethylene or acetylene bonds, then in the case of vinylalkylacetylenes and isopropenylacetylene the double bond must be enriched with electrons. Actually, these hydrocarbons give mainly acetylene dibromides. The triple bond in molecules of alkenylacetylenes (as well as vinylacetylene) must be enriched with electrons. This may be the cause of bromine addition to these substances at the 1,4-position, probably with the initial attack at the acetylene bond and completion of the fixation of the second bromine atom at the ethylene bond.

The existence of the hypothetical electronic displacements in molecules of vinylacetylene hydrocarbons was confirmed by measurement of the interatomic distances and is in agreement with the infrared spectra of these materials [9].

The rules on the order of bromine addition to vinylacetylene hydrocarbons examined above are of interest for the general theory of double and triple bonds, which is under consideration at present. Our experiments did not confirm Bohlmann's [10] opinion on the nucleophilic character of bromine addition at the triple bond. The triple bond becomes more reactive in relation to bromine when enriched with electrons, which indicates an electrophilic character for its reaction with bromine. We propose to discuss this problem in subsequent reports.

EXPERIMENTAL

The preparation methods and constants of the vinylacetylene hydrocarbons used in this work were given previously [1,9]. For bromination, we used substances boiling over ranges of 0.5-1°, stabilized with hydroquinone.

Bromination of propenylacetylene.* A solution of 13.2 g of propenylacetylene in 100 ml of chloroform was treated with 21.8 g of bromine in 30 ml of chloroform with stirring and cooling (-10 to 0°) and as a result of distilling the mixture in vacuum, we obtained 26 g (84% on the bromine) of dibromides and 4.3 g of residue.

Dibromides (1,4-dibromopentadiene-1,2 with traces of 1,2-dibromopentadiene-1,3). B.p. 66-76° (10 mm) d_4^{20} 1.7926, n_D^{20} 1.5742, MR 41.60 $C_5H_6Br_2$ $\bar{F}_2$. Calculated 39.89.

Found %: Br 70.63, 70.82. $C_5H_6Br_2$. Calculated %: Br 70.74.

Infrared spectra**: 3.24* (strong), 3.26 (strong), 3.34 (strong), 3.43 (strong), 3.52 (strong), 3.69 (weak), 4.10 (weak), 4.35 (weak), 5.09 (strong), 5.42 (weak), 5.82 (medium), 6.10 (strong), 6.40 (strong), 6.56* (medium), 6.94 (strong), 7.16 (strong), 7.31 (strong) μ (Fig. 1, Curve 1).

On treating 9 g of dibromide with 3 g of KOH in 30 ml of methyl alcohol in the cold for 2 hours, 2.0 g of bromide ion was formed, representing 32 % of the bromine present in the dibromide (with another sample of dibromide under the same conditions, 38 % of the bromine went into solution). By diluting the mixture with water an oil was isolated, which was washed with $CaCl_2$ solution, dried and separated into two parts by distillation: the 1st was vinylbromoacetylene, 1.6 g; the 2nd was a diene dibromide (with an ether impurity), 3.2 g.

For the vinylbromoacetylene (mainly 1-bromopenten-3-ine-1) we found:

B. p. 45-47° (40 mm), d_4^{20} 1.3785, n_D^{20} 1.5210, MR 32.03; Calc. 30.59.

Found %: Br 54.61, 54.44. C_5H_5Br. Calculated %: Br 55.11.

Infrared spectrum: 3.03 (weak), 3.28 (strong), 3.35 (strong), 3.39 (strong), 3.44 (strong), 3.51 (strong), 3.67 (very weak), 3.97 (very weak), 4.07 (very weak), 4.18 (very weak), 4.38 (very weak), 4.52 (strong), 4.83 (weak), 5.82 (weak), 5.47 (weak), 5.74 (medium), 5.95 (medium), 6.13 (medium), 6.91 (strong), 7.13 (strong), 7.31 (strong) μ (Fig. 1, Curve 3).

For the 1,2-dibromopentadiene-1,3, with the ether impurity, we found:

B. p. 62-66° (10 mm), d_4^{20} 1.7630, n_D^{20} 1.5719.

Found %: Br 68.88; OCH_3 1.31. $C_5H_6Br_2$. Calculated %: Br 70.74.

By heating 8.2 g of the original dibromide with 6 g of Cu_2Br_2 and 15 ml of concentrated hydrobromic acid in 30 ml of ether on a water bath for 5 hours, we obtained 5 g (60 %) of 1,2-dibromopentadiene-1,3.

B. p. 60-62° (10 mm), d_4^{20} 1.8079, n_D^{20} 1.5670, MR 40.82; Calc. 39.89.

Found %: Br 71.08, 71.14. $C_5H_6Br_2$. Calculated %: Br 70.74.

On treating this dibromide with a solution of KOH under the conditions given previously, bromine was not eliminated.

Infrared spectrum: 3.23 (strong), 3.29 (strong), 3.35 (strong), 3.40 (strong), 3.44 (strong), 3.52 (medium), 3.68 (very weak), 4.02 (very weak), 4.18 (very weak), 4.63 (very weak), 5.02 (very weak), 5.44 (weak), 5.74 (weak), 5.86 (weak), 6.08 (strong), 6.41 (medium), 6.57 (medium), 6.94 (strong), 7.16 (medium), 7.31 (strong) μ (Fig. 1, Curve 2).

Bromination of butenylacetylene. By treating a solution of 6.1 g of butenylacetylene in 100 ml of chloroform with 7 g of bromine in 20 ml of chloroform under the conditions given previously, we obtained 8 g of dibromide and 2 g of residue.

Dibromides (1,4-dibromohexadiene-1,2, with traces of 1,2-dibromopentadiene-1,3). B.p. 85-95° (10 mm) d_4^{20} 1.6937, n_D^{20} 1.5650, MR 46.15. $C_6H_8Br_2$ $\bar{F}_2$. Calculated 44.50.

* A mixture of cis and trans forms with a predominance of the former [11].

** The infrared transmission spectra of the dibromides were plotted with the help of G. I. Semenov on an IKS-2 spectrograph, in the range up to 5.5μ with a LiF prism and then with an NaCl prism, using a layer 0.1 mm thick. If the conditions were different, they are specifically indicated. The authors would like to thank G. I. Semenov for his help.

The asterisks indicate frequencies, which are superimposed on other, more intense frequencies.

Infrared spectrum (NaCl prism): 3.30 (strong), 3.40 (strong), 5.09 (strong), 5.82 (medium), 6.08 (medium), 6.37 (medium), 6.83 (strong), 7.20 (strong), 7.50 (strong) μ (Fig. 1, Curve 4).

On keeping 0.5 g of the dibromide for 2 hours with a solution of 0.2 g of KOH in 10 ml of alcohol, about 42 % of the bromine in the sample, went into solution.

On heating 4.7 g of the dibromide in 30 ml of ether with 14 ml of concentrated hydrobromic acid and 5 g of Cu_2Br_2, we obtained 1,2-dibromohexadiene-1,3.

B. p. 85-90° (10 mm), d_4^{20} 1.7092, n_D^{20} 1.5622, MR 45.54; Calc. 44.50.

Found %: Br 66.26, 66.53. $C_6H_8Br_2$. Calculated %: Br 66.61.

Infrared spectrum: 3.24 (medium), 3.31* (medium), 3.37 (strong), 3.44 (strong), 3.49 (strong), 3.54* (medium), 3.65 (weak), 5.52 (weak), 5.85 (strong), 6.10 (strong), 6.36 (medium), 6.52 (medium), 6.87 (strong), 7.10* (medium), 7.26 (medium), 7.53 (strong), 7.83 (strong) μ (Fig. 1, Curve 5).

Bromination of isopropenylacetylene. Under the usual conditions we obtained: a dibromide (1,2-dibromo--2-methylbutine-3) with b.p. 51-53° (10 mm) (d_4^{20} 1.7655, n_D^{20} 1.5349, MR 39.83; Calc. 38.82), a small fraction with b.p. 70-80° (10 mm) and a residue (tetrabromides).

Infrared spectrum of dibromide with b.p. 51-53° (10 mm): 3.03 (strong), 3.21* (medium), 3.25 (strong), 3.35 (strong), 3.43 (strong, 3.48* (strong), 3.68 (weak), 4.23 (weak), 4.67 (weak), 5.09 (weak), 5.41 (weak), 5.87 (weak), 6.03 (medium), 6.22 (medium), 6.78 (strong), 7.27 (strong) μ (Fig. 2, Curve 1).

Infrared spectrum of fraction 70-80° (20 mm) (NaCl prism, layer 0.1 mm thick)**: 3.03 (medium), 3.40 (medium), 4.74 (weak), 5.10 (medium), 5.81 (strong), 6.35 (strong), 6.90 (strong), 7.27 (strong) μ (Fig. 2, Curve 1 – dotted).

Bromination of 3-methylpenten-3-ine-1. From 19 g of hydrocarbon in 150 ml of cloroform and 12 g of bromine in 50 ml of chloroform, we obtained 7 g of dibromide and 9.5 g of residue.

Dibromides (a mixture of 1,4-dibromo-3-methylpentadiene-1,2, 1,2-dibromo-3-methylpentadiene-1,3 and 3,4-dibromo-3-methylpentine-1).

B. p. 70-85° (10 mm), d_4^{20} 1.6857, n_D^{20} 1.5548, MR 45.67. $C_6H_8Br_2$. Calculated 44.50. $C_6H_8Br_2$. Calculated 43.44.

Found %: Br 66.34, 66.49. $C_6H_8Br_2$. Calculated %: Br 66.61.

Infrared spectrum 3.03 (strong), 3.21* (medium), 3.25 (strong), 3.35 (strong), 3.43 (strong), 3.48* (strong), 3.68 (weak), 4.23 (weak), 4.67 (weak), 5.09 (strong), 5.41 (weak), 5.87 (weak), 6.03 (medium), 6.22 (medium), 6.78 (strong), 7.27 (strong) μ (Fig. 2, Curve 2).

On treating 0.537 g of dibromides with a solution of 0.2 g of KOH in 10 ml of methanol for 4 hours, 0.144 g of bromine went into solution, corresponding to 40 % of that in tha sample.

On heating 4.5 g of the dibromides in 30 ml of ether with 15 ml of concentrated hydrobromic acid and 5 g of Cu_2Br_2 for 5 hours on a water bath, we obtained a mixture of dibromides (mainly 1,2-dibromo-3-methylpentadiene-1,3):

B. p. 65-67° (10 mm), d_4^{20} 1.6636, n_D^{20} 1.5389, MR 45.18; Calc. 44.50

Found %: Br 66.08, 66.24. $C_6H_8Br_2$. Calculated %: Br 66.61

Infrared spectrum: 3.03 (medium), 3.23 (medium), 3.36 (strong), 3.41 (strong), 3.44 (strong), 3.48* (strong), 3.52* (medium), 3.68 (weak), 4.67 (weak), 5.09 (medium), 5.32 (weak), 5.81 (medium), 6.01 (medium), 6.24 (medium), 6.89 (strong), 7.26 (strong) μ.

Bromination of tert.-butylvinylacetylene. On brominating 19.3 g of hydrocarbon in 150 ml of chloroform with 18 g of bromine in 50 ml of chloroform, we obtained 20 g of dibromides, 2.7 g of a fraction with b.p. 105-110° (10 mm) and 11.7 g of residue (polybromides).

**Only the positions of the main frequencies were determined.

Dibromides (mainly 1,2-dibromo-1',1'-methyl-3-ethylbutadiene-1,3).

B. p. 83-93°, d_4^{20} 1.5285, n_D^{20} 1.5239, MR 54.89. $C_8H_{12}Br_2F_2$. Calculated 53.74.

Found %: Br 59.78, 59.32. $C_8H_{12}Br_2$. Calculated %: Br 59.64.

Infrared spectrum: 3.03 (strong), 3.35 (strong), 3.44* (strong), 3.69 (weak), 3.75 (weak), 3.91 (weak), 4.06 (weak), 4.18 (weak), 4.33 (weak), 4.45 (very weak), 4.68 (weak), 5.09 (weak), 5.40 (weak), 5.79* (weak), 6.17 (medium), 6.28 (strong), 6.78 (strong), 7.22 (strong), 7.30 (strong) μ (Fig. 2, Curve 3).

Fraction with b.p. 105-110° (10 mm), d_4^{20} 1.5763, n_D^{20} 1.5362.

Found %: Br 60.46. $C_8H_{12}Br_2$. Calculated %: Br 59.64.

The infrared spectrum of this fraction differed from the spectrum of the main fraction in a more intense frequency 5.09 μ and weaker frequencies 3.03 and 4.68 μ.

On treating 0.673 g of the fraction 83-93° (10 mm) with a twofold excess of 10 % KOH in methanol in the cold, there was noticeable KBr separation only after two days. On boiling the same mixture on a water bath for 45 minutes, 0.112 g of bromine went into solution, corresponding to 27 %, calculated on 1 atom of bromine.

On heating the same fraction (10 g) in an ether solution with hydrobromic acid and Cu_2Br_2, we obtained a product with a narrower boiling range, the main part of which had the constants:

B.p. 83-86° (10 mm), d_4^{20} 1.5142, n_D^{20} 1.5208, MR 53.88; Calc. 53.74.

Found %: Br 59.41. $C_8H_{12}Br_2$. Calculated %: Br 59.64.

The infrared spectrum of the substance differed from the spectrum of the original dibromide in the absence of the frequency 5.09 μ, a weakening of the frequency 3.03 and a strengthening of the frequency 6.24 μ.

0.32 g of the original fraction of dibromides was ozonized and in two samples (each one fifth of the total) of the ozonides we found 0.0044 and 0.0042 g of formaldehyde (determined as dinaphtholmethane), which corresponds to a minimal diene dibromide content of 58-61 %.

Bromination of vinylethylacetylene. We investigate the dibromide previously described (1,2-dibromohexine-3) with b.p. 87-87.5° (10 mm), n_D^{20} 1.5472.

Infrared spectrum (NaCl prism): 4.44 (strong), 5.36 (weak), 5.09 (very weak), 6.18 (weak), 6.32 (very weak), 6.82 (strong), 7.25 (strong), 7.48 (strong), 7.57 (strong) μ (Fig. 2, Curve 4).

SUMMARY

1. We investigated the order of bromine addition to alkenylacetylenes (penten-3-ine-1and hexen-3-ine-1) and isoalkenylacetylenes (3-methylpenten-3-ine1 and 1',1'-dimethyl-3-ethylbuten-3-ine-1). Additional data were also obtained on the bromination of 3-methylbuten-3-ine-1 and hexen-1-ine-3.

2. It was shown that alkenylacetylenes add bromine mainly at the 1,4-position with the formation of allene dibromides, which when treated with alcoholic alkali, give alkylbromoacetylenes and when treated with hydrobromic acid and Cu_2Br_2 give 1,3-diene dibromides.

3. It was established that the order of bromine addition to tert-butylvinylacetylene changes, in comparison with isopropenylacetylene, towards increased formation of 1,3-diene dibromide.

4. It was shown that a hydrocarbon with radicals, of opposing effects, on a conjugated system — 3-methylpenten-3-ine-1 gives a mixture of all three possible isomeric dibromides, with a predominance of the allene.

5. We used infrared spectra for establishing the structure of the dibromides of vinylacetylene hydrocarbons, enumerated above and some described previously.

6. We put forward the hypothesis that all the rules established for the reactions of vinylacetylene hydrocarbons with bromine may be explained by the theory of electronic displacement.

* Only the positions of the main frequencies were determined.

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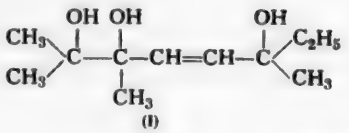
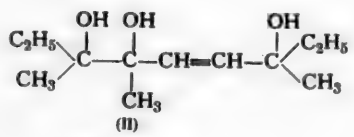
TERTIARY TRIATOMIC ALCOHOLS OF THE ACETYLENE SERIES AND THEIR REACTIONS

XI. HYDROGENATION OF 2,3,6-TRIMETHYLOCTINE-4-TRIOL-2,3,6; 3,4,7-TRIMETHYLNONINE-5-TRIOL-3,4,7 AND 2,4-DI-(1-HYDROXYCYCYCLOPENTYL--BUTIN-3-OL-2

V. I. Nikitin and I. M. Timofeeva

In this article we describe the synthesis of three new examples of tertiary, triatomic alcohols of the ethylene series – 2,3,6-trimethyloctene-4-triol-2,3,6 (I), 3,4,7-trimethylnonene-5-triol-3,4,7 (II) and 2,4-di-(1-hydroxycyclopentyl)-buten-3-ol-2 (III) and give data on the investigation of the hydrogenation rate of 2,3,6-trimethyloctine-4-triol-2,3,6 (IV), 3,4,7-trimethylnonine-5-triol-3,4,7 (V) and 2,4-di-(1-hydroxycylocopentyl)-butin-3--ol-2 (VI).


(I)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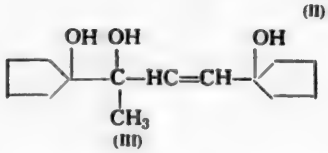
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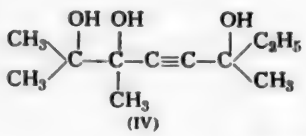
We prepared the triols by catalytic hydrogenation of the appropriate tertiary triatomic alcohols of the acetylene series (IV, V and VI).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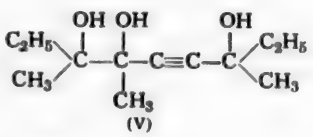
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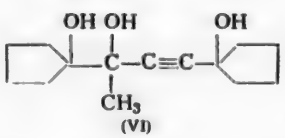
(VI)

As noted in one of our previous reports [1], tertiary glycerins of the acetylene series were hydrogenated over both palladium and platinum catalysts with unusual selectivity, to glycerins of the ethylene series, after which the hydrogenation rate decreased sharply and almost stopped. This behavior was also confirmed for glycerins of the acetylene series (IV, V and VI), whose hydrogenation rate was investigated in this paper. We isolated 90 % and

greater yields of the corresponding ethylene glycerins (I), (II) and (III), which as we indicated in the first report [1], should be considered sterically as the cis-form.

The picture of the hydrogenation rate of the acetylene glycerins given above, is shown by appropriate curves (Figs. 1,2 and 3), plotted according to S. V. Lebedev's method (time in minutes – along the abscissa and the amount of hydrogen, in milliliters, consumed per minute – along the ordinate).

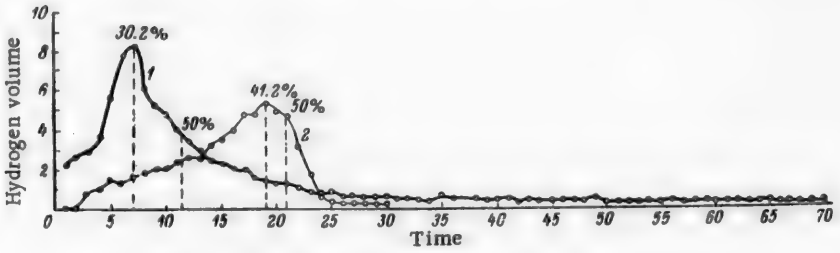

Fig. 1. Hydrogenation of 2,3,6-trimethyloctine-4-triol-2,3,6 (IV).
1) With 0.006 g of platinum oxide (27°), 2) with 0.008 g of palladium (27°).

In all cases the same amount of material was taken for hydrogenation: 0.002 mole of the alcohol being hydrogenated and the following amounts of catalysts: platinum oxide calculated at 3 g per mole of the alcohol being hydrogenated, palladium, deposited on chalk, calculated at 4 g of prepared catalyst per mole of alcohol*. The experiments were carried out at a pressure of 688.5 mm, with the exception of the hydrogenation of 3,4,7-trimethylnonine-5-triol-3,4,7 (V) in the presence of palladium (see curve 2, Fig. 3), where the experiment was carried out at a pressure of 689 mm.

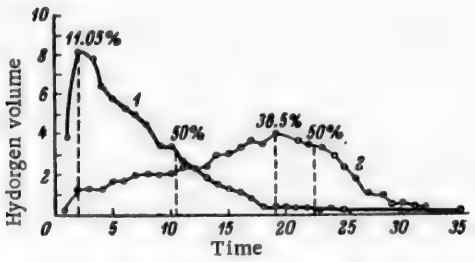

Fig. 2. Hydrogenation of 3,4,7-trimethylnonine-5-triol-3,4,7 (V).
1) With 0.006 g of platinum oxide (27°),
2) With 0.008 g of palladium (27°)

Hydrogenation was carried out in the usual "duck;"** placed on a rocker. Methanol (10 ml), first distilled over caustic alkali, was used as the solvent. The hydrogen was read off from a buret of 100 ml capacity (H_2 54.8 ml, $2H_2$ 109.8 ml).

An examination of the curves given shows that over a platinum catalyst, 2,4-di-(1-hydroxycyclopentyl)-butinol (VI) was hydrogenated the most rapidly. Hydrogenation of this triol to the double bond was complete in 6 minutes, while trimethyloctinetriol (IV) required more than 11 minutes for this; the hydrogenation of trimethylnoninetriol (V) to the double bond also proceeded at the same rate (about 11 minutes) over a platinum catalyst.

On the contrary, over a palladium catalyst, the hydrogenation rate of the series of glycerins investigated was least for 2,4-di-(1-hydroxycyclopentyl)-butinol (VI) (65 minutes), while at the same time it was considerably greater for trimethyloctinetriol (IV) and trimethylnoninetriol (V) and the reaction took 21-22 minutes.

EXPERIMENTAL

1. Synthesis of 2,3,6-trimethyloctene-4-triol-2,3,6 (I)

The starting 2,3,6-trimethyloctine-4-triol-2,3,6 (IV) was prepared by condensation of dimethylacetylcar-

* In synthesizing ethylene glycerines (see Experimental), when larger amounts of acetylene glycerin were used in the reaction, the ratio between the catalyst and triol being hydrogenated had to be changed, using a smaller amount of catalyst, due to the violence of the reaction.

** Hydrogenation flask — Publisher's note.

binol with methylethylacetylenylcarbinol [2] and had b.p. 121-122° (1.5 mm), m.p. 57-59°, which corresponds to the literature data.

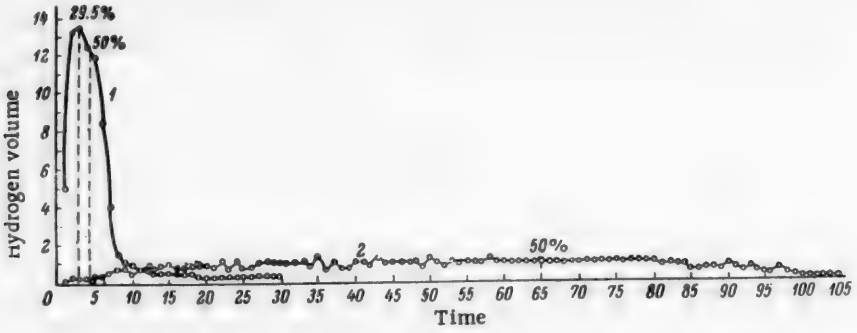

Fig. 3. Hydrogenation of 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 (VI).
1) With 0.006 g of platinum oxide (27°), 2) with 0.008 g palladium (25°).

a) Hydrogenation over a platinum catalyst. 5.8 g of 2,3,6-trimethyloctine-4-triol-2,3,6 was hydrogenated over 0.08 g of platinum oxide in 60 ml of methanol at 24° and 689.6 mm. The calculated amount of hydrogen for hydrogenation to the double bond (778.8 ml) was passed in 35 minutes, after which the hydrogenation was stopped. The catalyst was filtered off and the solvent distilled off. The product was dissolved in ether and dried over potash. The ether was distilled off and the product distilled in vacuum. We distilled over 5.0 g of substance (85.5%), which was a glycerin of the ethylene series, not previously described in the literature – cis-2,3,6-trimethyloctene-4-triol-2,3,6.

B. p. 114-115° (2 mm), d_4^{20} 1.0028, n_D^{20} 1.4757, MR_D 56.78. $C_{11}H_{22}O_3$. Calculated 57.11.

b) Hydrogenation over a palladium catalyst. 5 g of 2,3,6-trimethyloctine-4-triol-2,3,6, dissolved in 60 ml of methanol, was hydrogenated over 0.1 g of palladium on chalk at 28° and 689.2 mm. The calculated amount of hydrogen for hydrogenation to the double bond (680.8 ml) was passed in 30 minutes.

After the absorption of the theoretical amount of hydrogen, the hydrogenation was stopped and the product was treated similarly to the previous one and distilled in vacuum. We obtained 4.8 g of a substance (95.0 %) which was also cis-2,3,6-trimethyloctene-4-triol-2,3,6. The b.p. was 114-115° (2 mm), n_D^{20} 1.4757.

Found %: C 65.20, 65.38; H 10.63, 10.59; OH 24.54, 24.96. $C_{11}H_{22}O_3$. Calculated %: C 65.35; H 10.9; OH 25.2.

2. Synthesis of 3,4,7-Trimethylnonene-5-Triol-3,4,7 (II)

3,4,7-Trimethylnonine-5-triol-3,4,7 (V) was prepared by condensation of methylethylacetylcarbinol with methylethylacetylenylcarbinol [2] and had b.p. 124-126° (2 mm), n_D^{20} 1.4810, which corresponds to the literature data.

a) Hydrogenation over a platinum catalyst. 5 g of 3,4,7-trimethylnonine-5-triol-3,4,7 was hydrogenated over 0.07 g of platinum oxide in 60 ml of methanol at 23° and 690.7 mm. In 18 minutes the calculated amount of hydrogen (630.0 ml) was consumed. After this the reaction was stopped. The catalyst was filtered off and the alcohol distilled off. The product was dissolved in ether and dried with potash. The ether was distilled off and the product distilled in vacuum. We distilled off 4.8 g of a substance (95.2 %), which was a glycerin of the ethylene series, not previously described in the literature – cis-3,4,7-trimethylnonene-5-triol-3,4,7.

B. p. 126-127° (2 mm), d_4^{20} 0.9977, n_D^{20} 1.4790, MR_D 61.41. $C_{12}H_{24}O_3$. Calculated 61.72.

b) Hydrogenation over a palladium catalyst. 5 g of 3,4,7-trimethylnonine-5-triol-3,4,7 was hydrogenated over 0.09 g of palladium in 60 ml of methanol at 21° and 692.5 mm. The calculated amount of hydrogen for hydrogenation to the double bond (630 ml) was consumed in 30 minutes, after which the hydrogenation was stopped. The product was treated similarly to the previous one and distilled in vacuum. We obtained 4.8 g (95.2 %) of a

substance, which was also cis-3,4,7-trimethylnonene-5-triol-3,4,7. The b.p. was 126-127° (2 mm), n_D^{20} 1.4790.

Found %: C 66.99, 66.25; H 11.12, 11.06; OH 23.13. $C_{12}H_{24}O_3$. Calculated %: C 66.66; H 11.11; OH 23.82.

3. Synthesis of 2,4-Di-(1-Hydroxycyclopentyl)-Buten-3-Ol-2 (III)

The starting 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 (VI) was prepared by condensation of acetylcyclopentanol with acetylenylcyclopentanol. The m.p. was 93-94°, which corresponds to the literature data [2].

a) Hydrogenation over a platinum catalyst. 10 g of 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 was hydrogenated in the presence of 0.1 g of platinum oxide in 60 ml of methanol at 27° and 689.1 mm. The calculated amount of hydrogen for hydrogenation to the double bond (990 ml) was absorbed in 30 minutes, after which the reaction was stopped. The catalyst was filtered off, the alcohol distilled off from the reaction products and the remaining product crystallized on standing. When recrystallized several times from ethyl alcohol or ethyl ether it melted at 129-130°. We obtained 9.2 g (91.2 %).

b) Hydrogenation over a palladium catalyst. 10 g of 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 was hydrogenated in the presence of 0.15 g of palladium on chalk in 60 ml of methanol at 27° and 689.1 mm. The calculated amount of hydrogen for hydrogenation to the double bond was 990 ml and was absorbed in 45 minutes, after which the reaction slowed down considerably and was stopped. The catalyst was filtered off, the alcohol distilled off from the reaction products and the remaining product crystallized on standing. After several recrystallizations from ethyl alcohol, we obtained 9.4 g (92.2 %) of a substance with m.p. 129-130°. The crystals isolated from the hydrogenation of 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 over platinum and palladium catalysts, were identical (established by a mixed melting point) and were cis-2,4-di-(1-hydroxycyclopentyl)-buten-3-ol-2, which has not been described in the literature.

Found %: C 70.17, 70.07; H 10.16, 10.19; OH 20.62, 20.66. $C_{14}H_{24}O_3$. Calculated %: C 70.00; H 10.00; OH 21.20.

SUMMARY

1. Tertiary glycerins of the acetylene series — 2,3,6-trimethyloctine-4-triol-2,3,6; 3,4,7-trimethylnonine-5-triol-3,4,7 and 2,4-di-(1-hydroxycyclopentyl)-butin-3-ol-2 were hydrogenated in the presence of both platinum and palladium catalysts to the corresponding glycerins of the ethylene series, apparently giving sterically only the one cis-form.

2. We synthesized the following glycerins of the ethylene series: 2,3,6-trimethyloctene-4-triol-2,3,6; 3,4,7-trimethylnonene-5-triol-3,4,7 and 2,4-di-(1-hydroxycyclopentyl)-buten-3-ol-2.

LITERATURE CITED

[1] V. I. Nikitin and I. M. Timofeeva, J. Gen. Chem. 25, 1334 (1955).*

[2] V. I. Nikitin and S. D. Savranskaya, J. Gen. Chem. 25, 1106 (1955).*

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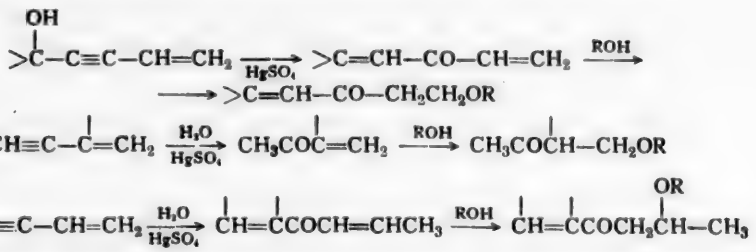
* Original Russian pagination. See C. B. Translation.

ACETYLENE DERIVATIVES

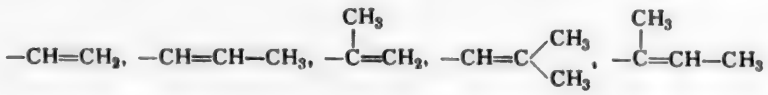
184. SYNTHESIS AND CONVERSIONS OF β-ACETOXYKETONES

I. N. Nazarov, S. G. Matsoyan and S. A. Vartanyan

It was shown in previous reports from our laboratory [1] that in isomerizing vinylacetylene alcohols and in hydrating vinylacetylene and divinylacetylene hydrocarbons in alcohol solutions in the presence of mercury salts, the corresponding β-alkoxyketones were formed as the final products.

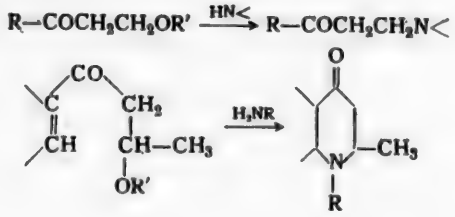


All these reactions proceeded in two stages: first α,β-unsaturated ketones were formed which readily added alcohols under the experimental conditions and were converted into the corresponding β-alkoxyketones. The rate of alcohol addition to the double bonds of α,β-unsaturated ketones depended greatly on substitution and decreased with the introduction of substituents in the vinyl radical in the following order:



The ordinary disubstituted ketovinyl groups were completely incapable of adding alcohol or secondary amines under the given conditions.

When treated with aqueous solutions of ammonia and primary and secondary amines the β-alkoxyketones readily underwent aminolysis to give β-aminoketones and γ-piperidones, which are important starting materials for the synthesis of anesthetics [2].



It is shown in the present work, that β-alkoxyketones are also capable of acidolysis reactions.

Thus, for example, heating methyl β-methoxyethyl ketone with acetic acid and acetic anhydride in the presence of sodium acetate gave methyl β-acetoxyethyl ketone (I), and about 60% yield, together with an equivalent amount of methyl acetate.

$$CH_3COCH_2CH_2OCH_3 \xrightarrow[(CH_3CO)_2O]{CH_3COOH} \underset{(I)}{CH_3COCH_2CH_2OCOCH_3} + CH_3COOCH_3$$

Methyl β-acetoxyethyl ketones were also formed in 55-60% yield by hydrating vinylacetylene in a solution of acetic acid in the presence of mercuric acetate or by adding acetic acid directly to already prepared methyl vinyl ketone:

$$CH{\equiv}C{-}CH{=}CH_2 \xrightarrow[Hg(OCOCH_3)_2]{H_2O} CH_3COCH{=}CH_2 \xrightarrow{CH_3COOH} CH_3COCH_2CH_2OCOCH_3$$

The acidolysis of other more complicated β-alkoxyketones, containing, in particular, double bonds, proceeded just as readily. Heating the unsaturated β-methoxyketones (II) and (III) with acetic acid and acetic anhydride in the presence of sodium acetate gave the corresponding β-acetoxyketones (IV) and (V) in 55-65 % yields.

$$\underset{\text{(II) } R=H;\ \text{(III) } R=CH_3}{CH_3\overset{R}{\overset{|}{C}}{=}CHCOCH_2CH_2OCH_3} \xrightarrow[(CH_3CO)_2O]{CH_3COOH} \underset{\text{(IV) } R=H;\ \text{(V) } R=CH_3}{CH_3\overset{R}{\overset{|}{C}}{=}CHCOCH_2CH_2OCOCH_3} + CH_3COOCH_3$$

On hydrogenating the unsaturated β-acetoxyketones (IV) and (V) in the presence of a Pt-catalyst, the theoretical amount of hydrogen was absorbed (1 mole), and the corresponding saturated β-acetoxyketones (VI) and (VII) were formed.

$$\underset{(VI)}{CH_3CH_2CH_2COCH_2CH_2OCOCH_3} \qquad \underset{(VII)}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2COCH_2CH_2OCOCH_3}$$

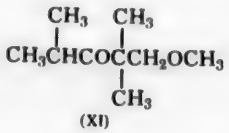
Acetolysis of 1,5-dimethoxyhexan-3-one (VIII), besides the normal reaction product – 1,5-diacetoxyhexan-3-one (IX) (in 15 % yield), resulted mainly in the formation of the unsaturated β-acetoxyketone (IV) described above (in 50 % yield).

$$\underset{(VIII)}{CH_3\overset{OCH_3}{\overset{|}{C}}HCH_2COCH_2CH_2OCH_3} \xrightarrow[(CH_3CO)_2O]{CH_3COOH} \underset{(IX)}{CH_3\overset{OCOCH_3}{\overset{|}{C}}HCH_2COCH_2CH_2OCOCH_3} + (IV)$$

Acetolysis of 1,5-dimethoxy-5-methylhexan-3-one (X) gave only the unsaturated β-acetoxyketone (V) described above in about 70% yield, while the corresponding diacetoxyketone did not form at all.

$$\underset{(X)}{CH_3\overset{CH_3}{\overset{|}{\underset{OCH_3}{\overset{|}{C}}}}CH_2COCH_2CH_2OCH_3} \xrightarrow[(CH_3CO)_2O]{CH_3COOH} (V)$$

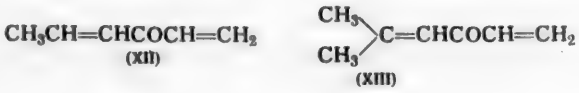
Thus, the acidolysis reaction proceeded normally with the substitution of the alkoxyl group by an acetoxy group, only in the case of the primary and partially, the secondary β-alkoxyketones, while at the same time the tertiary β-alkoxyl groups were eliminated in the form of alcohols with the formation of a double bond. Apparently, this process of alcohol elimination from β-alkoxyketones is connected with the mechanism of the acidolysis reaction (as well as aminolysis), as 1-methoxy-2,2,4-trimethylpentan-3-one (XI) is incapable of forming a α,β--double bond, and is completely incapable of acidolysis reactions (as well as aminolysis) and is recovered unchanged from these reactions.



(XI)

Acetic acid was added to α,β-unsaturated ketones under the conditions of acetolysis, with the formation of the corresponding β-acetoxyketones. An unsubstituted vinyl group adds acetic acid most readily, a propenyl group adds acetic acid with great difficulty, while a β,β-dimethylvinyl group is completely incapable of this addition. Therefore, only vinylacetylene itself is hydrated comparatively readily in an acetic acid solution while the substituted vinylacetylenes, formed during hydration, are incapable of adding acetic acid and substituted vinyl ketones cannot even be hydrated under these conditions.

Vinyl propenyl ketone (XII) added acetic acid in the presence of sodium or mercuric acetates with the formation mainly of the unsaturated acetoxyketone (IV) and a small amount (about 10 %) of the diacetoxyketone (IX), while at the same time an analogous reaction with β, β-dimethyldivinyl ketone (XIII) gave only the unsaturated acetoxyketone (V).



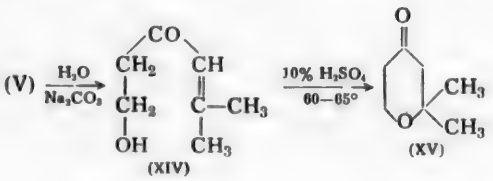
(XII) (XIII)

The β-acetoxy group is distinguished by an extremely high lability and readily undergoes cleavage, hydrolysis, alcoholysis, aminolysis etc.

β-Acetoxyketones split off acetic acid with the formation of α,β-unsaturated ketones even when distilled at atmospheric pressure and especially readily in the presence of p-toluenesulfonic acid or zinc chloride.

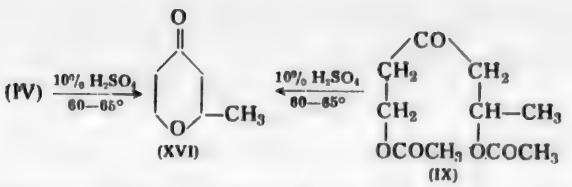
When hydrolyzed with an aqueous potash solution or 10 % sulfuric acid, methyl β-acetoxyethyl ketone (I) was converted into the known 1-hydroxy-3-butanone [3].

Hydrolysis of 1-acetoxy-5-methyl-4-hexen-3-one (V) with an aqueous soda solution made it possible to isolate, besides the diene (XIII), the unsaturated β-ketoalcohol (XIV), which when heated with 10 % sulfuric acid was readily cyclize into 2,2-dimethyltetrahydro-4-pyrone (XV).



(XIV) (XV)

Heating the acetoxyketone (V) with 10 % sulfuric acid immediately gave the pyrone (XV) and the intermediate ketoalcohol (XIV) could not be isolated. In an analogous way the acetoxyketones (IV) and (IX) when heated with 10 % sulfuric acid were converted into 2-methyltetrahydro-4-pyrone (XVI).



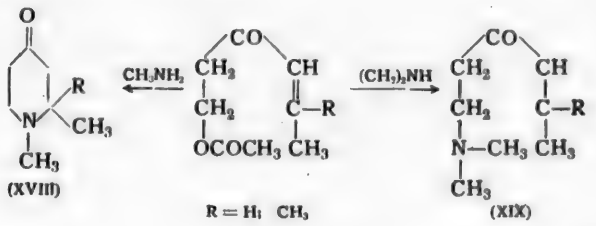
The intermediate ketoalcohols, under the conditions of acidic hydrolysis, could not be isolated in this case as well.

β-Acetoxyketones undergo aminolysis especially vigorously. Treatment of the β-acetoxyketones (I), (VI) and (VII) with an aqueous solution of dimethylamine produced an aminolysis reaction with strong heat evolution and the corresponding β-dimethylaminoketones (XVII) were formed in high yield.

$$R{-}COCH_2CH_2OCOCH_3 \xrightarrow{(CH_3)_2NH} \underset{(XVII)}{RCOCH_2CH_2N(CH_3)_2}$$

R=CH$_3$; n.-C$_3$H$_7$; изо-C$_4$H$_9$

The reaction of an aqueous solution of methylamine or dimethylamine with unsaturated β-acetoxyketones (IV) and (V) also proceeded with strong heat evolution and resulted in the formation of the corresponding γ-piperidones (XVIII) and unsaturated β-aminoketones (XIX).



Alcoholysis occurred readily when β-acetoxyketones were heated in alcohols containing traces of sulfuric acid and this gave the corresponding β-alkoxyketones in high yields.

$$R{-}COCH_2CH_2OCOCH_3 \xrightarrow{R'OH} RCOCH_2CH_2OR'$$

EXPERIMENTAL

Hydration of vinylacetylene in acetic acid. A mixture of 450 g of acetic acid and 5 g of mercuric acetate was heated to 60-80° and stirred for 8 hours while 95 g of vinylacetylene was passed in and at the same time 25 g of mercuric acetate in 110 g of 50 % acetic acid was added dropwise. The rate of addition of vinylacetylene was controlled with a Tishchenko bottle, connected to the end of the reflux condenser. The next day, after stirring the reaction mixture on a boiling water bath for 2 hours, the acetic acid was distilled off (45° at 25 mm) and the residue distilled in vacuum. After a second distillation we obtained 130 g of methyl β-acetoxyethyl ketone (I).

B.p. 80-82° (10 mm), 176-178° (680 mm with slight decomposition), n_D^{20} 1.4230, d_4^{20} 1.0417, MR 31.81. Calc. 31.57.

Found %: C 55.63, 55.67; H 8.13, 7.96. $C_6H_{10}O_3$. Calculated %: C 55.38; H 7.75.

After recrystallization from alcohol, the semicarbazone melted at 135-136°.

Found %: N 22.88. $C_7H_{13}O_3N_3$. Calculated %: N 22.46.

By treating methyl β-acetoxyethyl ketone with an aqueous alcohol solution of phenylhydrazine hydrochloride and sodium acetate and then heating on a water bath, we obtained the known 1-phenyl-3-methylpyrazoline [4] with m.p. 76-77° (from alcohol).

Addition of acetic acid to methyl vinyl ketone. A mixture of 5 g of methyl vinyl ketone, 15 g of glacial acetic acid and 1.5 g of mercuric acetate was heated under reflux on a boiling water bath for 5 hours. After distilling the reaction mixture in vacuum, we obtained 3.5 g of methyl β-acetoxyethyl ketone (I) with b.p. 100-103° (30 mm), n_D^{20} 1.423, whose semicarbazone melted at 136° and did not depress the melting point of the previous sample.

Acetolysis of methyl β-methoxyethyl ketone. A mixture of 50 g of methyl β-methoxyethyl ketone (b.p. 133-135° at 680 mm, n_D^{20} 1.404), 100 g of glacial acetic acid, 80 g of acetic anhydride and 5 g of anhydrous sodium acetate was heated on a metal bath at 120-130° for 8 hours (the temperature in the vapor was kept at 55-65°). After a second distillation of the distillate collected, we obtained 30 g of methyl acetate and 5 g of methyl vinyl ketone. The following day the excess acetic acid was distilled off in vacuum on a water bath (40-45°) and the residue treated with water, neutralized with sodium biearbonate, extracted with ether and dried with magnesium sulfate. On distilling the ether extract, we isolated 38.5 g of methyl β-acetoxyethyl ketone (I) with b.p. 82-84° (11 mm), n_D^{20} 1.4230, whose semicarbazone melted at 135-136°.

Under the same conditions the methoxyketone (XI) was not acetolized at all and was recovered unchanged.

Hydrolysis of methyl β-acetoxyethyl ketone. A mixture of 13 g of the acetoxyketone (I) (b.p. 80-81° at 10 mm, n_D^{20} 1.4230) and 28 g of 10 % sulfuric acid was stirred for 5 hours at 60-70°. The hydrolysis products were saturated with potash, extracted with ether and dried with magnesium sulfate. By distillation we isolated 6 g of 1-hydroxy-3-butanone [3].

B.p. 72-74° (10 mm), n_D^{20} 1.4310, d_4^{20} 1.0221, MR 22.32; Calc. 22.20.

Hydrolysis of the acetoxyketone (I) with an aqueous solution of potash also lead to 1-hydroxy-3-butanone. However, here the yield of the β-ketol was lower due to the formation of methyl vinyl ketone. On treating methyl β-acetoxyethyl ketone with an aqueous solution of potassium hydroxide, a vigorous polymerization occurred.

Acetolysis of 1-methoxy-4-hexen-3-one (II). A mixture of 50 g of the methoxy ketone (II) (b.p. 72-74° at 10 mm, n_D^{20} 1.4505) [1], 120 g of glacial acetic acid, 70 g of acetic anhydride and 5 g of anhydrous sodium acetate was heated at 120-135° for 7 hours so that the temperature of the vapor was maintained at 55-75°; thus we collected 22 g of methyl acetate (after a second distillation).

As a result of working up the residue similarly to the previous one, we obtained 36.5 g of 1-acetoxy-4-hexen-3-one (IV).

B. p. 75-77° (1 mm), 112-113° (10.5 mm), n_D^{20} 1.4580, d_4^{20} 1.0337, MR 41.15, Calc. 40.34.

Found %: C 61.30, 60.90; H 7.85, 8.13. $C_8H_{12}O_3$. Calculated %: C 61.51; H 7.74.

Acetolysis of 1,5-dimethoxyhexan-3-one (VIII). A mixture of 36 g of the dimethoxyketone (VIII) (b.p. 88-89° at 10 mm, n_D^{20} 1.4275) [1], 80 g of glacial acetic acid, 50 g of acetic anhydride and 4 g of sodium acetate was heated as above. Over 12 hours we collected 28 g of methyl acetate (after a second distillation). After working up the acetolysis product in the usual way, we obtained 17.5 g of 1-acetoxy-4-hexen-3-one (IV) with b. p. 75-77° (1 mm), n_D^{20} 1.4580 and 7.5 g of 1,5-diacetoxyhexan-3-one (IX).

B. p. 105-106° (1 mm), n_D^{20} 1.4420, d_4^{20} 1.0957, MR 52.20; Calc. 51.70.

Found %: C 55.71, 55.65; H 7.62, 7.40. $C_{10}H_{16}O_5$. Calculated %: C 55.50; H 7.41.

Addition of acetic acid to vinyl propenyl ketone. A mixture of 15 g of vinyl propenyl ketone (XII) (b.p. 36-39° at 10 mm, n_D^{20} 1.4730) [1], 45 g of glacial acetic acid and 2 g of mercuric acetate was boiled under reflux for 7 hours. After twice distilling the reaction mixture in vacuum, we obtained 10 g of 1-acetoxy-4-hexen-3-one (IV) with b.p. 75-77° (1 mm), n_D^{20} 1.4585 and 1.2 g of 1,5-diacetoxyhexan-3-one (IX). The b.p. was 104-106° (1 mm), n_D^{20} 1.4425.

Hydrogenation of 1-acetoxy-4-hexen-3-one (IV). 7 g of the material (b.p. 75-77° at 1 mm, n_D^{20} 1.4580), dissolved in 14 g of alcohol, was hydrogenated in the presence of Pt-catalyst. In all 1250 ml of hydrogen (17°, 680 mm) was consumed instead of 1220 ml required theoretically. By distillation in vacuum, we obtained 6.5 g of propyl β-acetoxyethyl ketone (VI).

B.p. 82-84° (5 mm), n_D^{20} 1.4280, d_4^{20} 0.9936, MR 20.96; calc. 40.81.

Found %: C 60.83, 60.81; H 9.21, 9.11. $C_8H_{14}O_3$. Calculated %: C 60.73; H 8.92.

The semicarbazone melted at 120.5-122° after recrystallization from 90 % alcohol.

Found %: N 19.95. $C_9H_{18}O_3N_3$. Calculated %: N 19.53.

Acetolysis of 1-methoxy-5-methyl-4-hexen-3-one (III). A mixture of 65 g of the methoxyketone (III) (b.p. 83-86° at 15 mm, n_D 1.4558) [1], 130 g of glacial acetic acid, 100 g of acetic anhydride and 6.5 g of anhydrous sodium acetate was heated at 120-135° and the temperature of the vapor was kept at 55-75°. Over a period of 7 hours we collected 25 g of methyl acetate.

As a result of the usual working up we obtained 50 g of 1-acetoxy-5-methyl-4-hexen-3-one (V).

B.p. 90-92° (2.5 mm), 114-116° (10 mm), n_D^{20} 1.4640, d_4^{20} 1.0200, MR 46.10; calc. 44.96.

Found %: C 63.66, 63.76; H 8.27, 8.57. $C_9H_{14}O_3$. Calculated %: C 63.53; H 8.29.

After recrystallization from alcohol or benzene, the semicarbazone melted at 133-134°.

Found %: N 18.57. $C_{10}H_{17}O_3N_3$. Calculated %: N 28.49.

Acetolysis of 1,5-dimethoxy-5-methylhexan-3-one (X). A mixture of 25 g of the dimethoxyketone (X) (b.p. 90-92° at 10 mm, n_D^{20} 1.4330) [5], 50 g of glacial acetic acid, 40 g of acetic anhydride and 3 g of anhydrous sodium acetate was heated as above. We obtained 16.5 g of 1-acetoxy-5-methyl-4-hexan-3-one (V) with b.p. 115-116° (10 mm), n_D^{20} 1.4640; the semicarbazone melted at 133-134° (from benzene).

Addition of acetic acid to β,β-dimethyldivinyl ketone (XIII). A mixture of 15 g of β,β-dimethyldivinyl ketone (XIII) (b.p. 43-45° at 10 mm, n_D 1.4820) [1], 35 g of glacial acetic acid and 1.5 g of anhydrous sodium acetate was boiled under reflux for 5 hours. After distilling off the acetic acid in vacuum on a water bath at 40°, the residue was treated with an aqueous solution of sodium bicarbonate and extracted with ether. We obtained 10.5 g of 1-acetoxy-5-methyl-4-hexen-3-one (V) with b.p. 90-91° (2.5 mm), n_D^{20} 1.4650; the semicarbazone melted at 133-134° and did not depress the melting point of the sample described above.

The reaction proceeded similarly in the presence of mercuric acetate.

Hydrogenation of 1-acetoxy-5-methyl-4-hexen-3-one (V). 8.5 g of the material (b.p. 115-116° at 10 mm, n_D^{20} 1.4640) was hydrogenated in 15 g of alcohol in the presence of Pt-catalyst. 1400 ml (20°, 680 mm) of hydrogen was consumed instead of 1380 ml, required theoretically. We obtained 8 g of 1-acetoxy-5-methylhexan-3-one (VII).

B. p. 90-92° (5 mm), n_D^{20} 1.4290, d_4^{20} 0.9715, MR 45.69; calc. 45.42.

Found %: C 62.35, 62.54; H 9.53, 9.54. $C_9H_{18}O_3$. Calculated %: C 62.77; H 9.36.

After recrystallization from 90 % alcohol, the semicarbazone melted at 137-138°.

Found %: N 18.81. $C_{10}H_{20}O_3N_3$. Calculated %: N 18.33.

Hydrolysis of 1-acetoxy-5-methyl-4-hexan-3-one (V). 10 g of sodium carbonate was dissolved in 30 ml of water and 15 g of the acetoxyketone (V) (b.p. 114-116° at 10 mm, n_D^{20} 1.464) added. The mixture was vigorously stirred for 4 hours at 65-75°. The hydrolysis products were extracted with ether, dried with magnesium sulfate and distilled in vacuum. We obtained 3.5 g of β,β-dimethyldivinyl ketone with b.p. 43-45° (10 mm), n_D^{20} 1.4825 and 4.5 g of 1-hydroxy-5-methyl-4-hexen-3-one (XIV).

B. p. 99-101° (10 mm), 63-65° (1 mm), n_D^{20} 1.4710, d_4^{20} 0.9995, MR 35.80; calc. 35.58.

Found %: C 65.85, 65.78; H 9.15, 9.32; OH 15.30. $C_7H_{12}O_2$. Calculated %: C 65.59; H 9.43; OH 13.28.

Cyclization of 1-hydroxy-5-methyl-4-hexen-3-one (XIV). A mixture of 3.5 g of ketoalcohol (XIV) (b.p. 99-101° at 10 mm, n_D^{20} 1.4710) and 20 g of 10 % sulfuric acid was vigorously stirred at 60-65° for 4 hours. The reaction mixture was saturated with potash, the product extracted with ether, dried and distilled in vacuum. We obtained 2.5 g of 2,2-dimethyltetrahydro-4-pyrone (XV) [6] with b.p. 62-64° (10 mm), n_D^{20} 1.4450; the semicarbazone melted at 165° and did not depress the melting point of an authentic sample.

Hydrolysis of 1-acetoxy-4-hexen-3-one (IV). A mixture of 8 g of acetoxyketone (IV) and 25 g of 10 %

sulfuric acid was stirred at 60-70° until the oily layer dissolved (4 hours). After working up in the usual way, we obtained 4 g of 2-methyltetrahydro-4-pyrone (XVI) [6] with b.p. 54-55° (10 mm), n_D^{20} 1.445; its semicarbazone melted at 169-170° and did not depress the melting point of an authentic sample.

Hydrolysis of 1-acetoxy-5-methyl-4-hexen-3-one (V). 8 g of the acetoxyketone (V) was hydrolyzed with 25 g of 10 % sulfuric acid at 60-70°, as described above. We obtained 4 g of 2,2-dimethyltetrahydro-4-pyrone (XV) with b.p. 61-64° (10 mm); the semicarbazone melted at 164-165°.

Hydrolysis of 1,5-diacetoxyhexan-3-one (IX). In the hydrolysis reaction we used 6 g of the diacetoxyketone (IX) (b.p. 104-105° at 1 mm, n_D^{20} 1.4420) and 18 g of 10 % sulfuric acid. We obtained 2 g of 2-methyltetrahydro--4-pyrone (XVI) with b.p. 57-60° (14 mm); the semicarbazone melted at 169°.

Methanolysis of methyl β-acetoxyethyl ketone (I). A mixture of 5 g of methyl β-acetoxyethyl ketone (b.p. 80-82° at 10 mm, n_D^{20} 1.4230) and 25 g of methanol, containing two drops of concentrated sulfuric acid, was boiled under reflux for 5 hours. The methanol was distilled off and the residue treated with an aqueous potash solution, extracted with ether and dried with magnesium sulfate. We obtained 3 g of methyl β-methoxyethyl ketone with b.p. 132-134° (680 mm), n_D^{20} 1.404; the 2,4-dinitrophenylhydrazone melted at 90-92° and did not depress the melting point of an authentic sample [1].

Ethanolysis of 1-acetoxy-5-methyl-4-hexen-3-one (V). A mixture of 8 g of acetoxyketone (V) (b.p. 115-116° at 10 mm, n_D^{20} 1.4645) and 30 g of ethanol, containing two drops of concentrated sulfuric acid, was boiled under reflux for 7 hours. It was then worked up as above. We obtained 5.5 g of 1-ethoxy-5-methyl-4-hexen-3-one [1] with b.p. 84-86° (10 mm), whose semicarbazone melted at 126-127° and did not depress the melting point of an authentic sample.

Aminolysis of β-acetoxyketones. a) 8 g of methyl β-acetoxyethyl ketone (I) and 33 g of aqueous dimethylamine (25%) were mixed in a round-bottomed flask. On shaking the flask, there was vigorous heat evolution and the ketoester quickly dissolved up. The following day, after the excess dimethylamine had been evaporated off in vacuum, the reaction mixture neutralized with hydrochloric acid (1:1) and the neutral product extracted with ether, the free base was separated with potash, extracted with ether, dried with magnesium sulfate and distilled in vacuum. We obtained 5.6 g of methyl β-dimethylaminoethyl ketone (XVII, R = CH_3) with b.p. 53-55° (18 mm), whose picrate melted at 108°, undepressed by admixture with an authentic sample [7].

b) Similarly, by reacting 3 g of propyl β-acetoxyethyl ketone (VI) (b.p. 82-84 at 4.5 mm, n_D^{20} 1.428) with 15 ml of aqueous dimethylamine, we obtained 2 g of propyl β-dimethylaminoethyl ketone (XVII, R = C_3H_7).

B. p. 70-71° (10 mm), n_D^{20} 1.4340, d_4^{20} 0.8643, MR 43.10; calc. 43.08.

After recrystallization from alcohol, the picrate melted at 104-105°.

Found %: N 15.96, 15.68. $C_{14}H_{20}O_8N_4$. Calculated %: N 15.60.

c) On treating 4 g of isobutyl β-acetoxyethyl ketone (VII) (b.p. 90-92° at 5 mm, n_D^{20} 1.4300) with 12 ml of aqueous dimethylamine as above, we obtained 2 g of isobutyl β-dimethylaminoethyl ketone (XVII, R = iso-C_4H_9) with b.p. 75-77° (11 mm), n_D^{20} 1.4325; the picrate melted at 99-101° (from alcohol) [2].

d) On treating 5 g of 1-acetoxy-5-methyl-4-hexen-3-one (V) (b.p. 114-116° at 10 mm, n_D^{20} 1.4645) with 18 ml of aqueous dimethylamine as above, we obtained 3.5 g of 1-dimethylamino-5-methyl-4-hexen-3-one (XIX, R = CH_3) with b.p. 85-88° (11 mm), n_D^{20} 1.465, whose picrate melted at 106-108° (from alcohol) [2].

e) On treating 8 g of 1-acetoxy-4-hexen-3-one (IV) (b.p. 75-77° at 1 mm, n_D^{20} 1.4580) with 25 ml of aqueous methylamine (25%), there was strong heat evolution and the β-ketoester dissolved. After working up in the usual way, we isolated 2 g of 2-methyl-4-piperidone (XVIII, R = H) with b.p 80-83° (10 mm), n_D^{20} 1.4586; the picrate melted at 163-164°, undepressed by admixture with an authentic sample [2].

SUMMARY

1. Heating β-methoxyketones with a mixture of acetic acid and acetic anhydride in the presence of sodium acetate gave the corresponding β-acetoxyketones in good yields. Methyl β-acetoxyethyl ketone was also prepared by direct hydration of vinylacetylene in a solution of acetic acid in the presence of mercuric acetate, as well as by the addition of acetic acid to methyl vinyl ketone.

2. The mechanism of acidolysis of β-methoxyketones consists, most probably, of the elimination of methanol with subsequent addition of acetic acid to the α, β-unsaturated ketone formed.

3. Acetic acid is readily added only by the unsubstituted ketovinyl group, while monosubstituted ketovinyl groups add it with great difficulty and disubstituted ones are incapable of adding acetic acid.

4. Hydrolysis of 1-acetoxy-5-methyl-4-hexen-3-one gave 1-hydroxy-5-methyl-4-hexen-3-one and it was cyclized into 2,2-dimethyltetrahydro-4-pyrone.

5. β-Acetoxyketones undergo aminolysis extremely readily when treated with aqueous solutions of ammonia and primary and secondary amines, with the formation of β-aminoketones and γ-piperidones. β-Acetoxyketones undergo alcoholysis readily when treated with alcohols, with the formation of β-alkoxyketones.

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INVESTIGATIONS OF AMINES AND QUATERNARY AMMONIUM COMPOUNDS

VII. REACTIONS OF HALOALKYL-CONTAINING TERTIARY AMINES AND THEIR METHIODIDES WITH ALKALI

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The difference between the dehydrochlorination rates of tertiary amines, containing a 3-chlorobuten-2-yl radical and their quaternary ammonium salts was reported earlier [1]. Dehydrochlorination of the amines with alcoholic alkali requires many hours of boiling [2], while at the same time the methiodides of these amines are readily dehydrochlorinated at 55° when treated with aqueous alkali [1].

Such a sharp difference in the reaction rate may be caused by a change in the stability of the halide or hydrogen bond in the 3-chlorobuten-2-yl radical or of both due to the change of the nitrogen from the amine into the ammonium state.

We undertook the investigation of tertiary amines and quaternary ammonium salts, containing polyhaloalkyls to find out the relation of the stability of bonds in amines, containing haloalkyls, and in their quaternary ammonium salts to the structure of the alkyl halide and character of the nitrogen, as well as to extend the dehydrochlorination-decomposition reaction [3] of quaternary ammonium salts to the synthesis of compounds with conjugated multiple bonds.

The present article is devoted to the reactions of 1-dimethylamino-2,3-dichlorobutane (I), 1,dimethylamino-2,3,3-trichlorobutane (II), 1,dimethylamino-2,2,3,3-tetrachlorobutane (III), 1-dimethylamino-3-chlorobutene-2 (IV), 1-dimethylamino-2,3-dichlorobutene-2 (V), 1-dimethylamino-2-chlorobutene-2 (VI) and the methiodides (Ia), (IIa), (IIIa), (IVa), (Va) with alkalies.

With the exception of (I) and (VI), these compounds have been described previously [4].

The starting material for the synthesis of substance (I) was 1-dimethylaminobutene-2 which was obtained as a second product in the isomerization of dimethylaminobutine-2 with metallic sodium [5]. Chlorination of the hydrochloride of 1-dimethylaminobutene-2 proceeded as well and as smoothly as chlorination of the hydrochlorides of dimethylaminobutine-2, 1-dimethylamino-3-chlorobutene-2 (IV) and dimethylamino-2,3-dichlorobutene-2 (V) [4]. We obtained the amine (VI) by the incomplete dehydrochlorination of amine (I).

The first molecule of hydrogen chloride in 2,3-dichlorobutane derivatives with a substitutent at the first carbon atom, suchas amine (I), had the following four possible ways of splitting off:

$$X{-}CH_2{-}CHCl{-}CHCl{-}CH_3 \longrightarrow \begin{cases} \xrightarrow{(a)} X{-}CH_2{-}CCl{=}CH{-}CH_3 \\ \xrightarrow{(b)} X{-}CH_2{-}CH{=}CCl{-}CH_3 \\ \xrightarrow{(a)} X{-}CH{=}CH{-}CHCl{-}CH_3 \\ \xrightarrow{(r)} X{-}CH_2{-}CHCl{-}CH{=}CH_2 \end{cases}$$

The first two reactions (a) and (b) are in agreement with Zaitsev's rule, but differ from each other in the directing effect of the substituent (X).

As is known, dehydrochlorination of 2,3-dichlorobutane itself proceeds in agreement with Zaitsev's rule and results in the formation of 2-chlorobutene-2 [6]. In investigating the effect of the nature of the substituent on the order of elimination of hydrogen chloride in compounds $X-CH_2-CHCl-CCl_2$, R. Kh. Freidlin, V. N. Kost and A. N. Nesmeyanov [7] showed that when $X = C_6H_5$, OCH_3 and $N(C_2H_5)_2$, compound $X-CH_2-CCl=CCl_2$ is formed as a result of dehydrochlorination, which agrees with Zaitsev's rule.

Our experiments on dehydrochlorination of (I) showed that there was a sharp difference between the elimination of the first hydrogen chloride molecule and the second. The elimination of the first molecule occurred even at room temperature, while the elimination of the second occurredonly after long boiling with solution of potassium hydroxide in polyethylene glycol. It was also shown that dimethylaminobutine-2 was formed as a result of full dehydrochlorination. None of this agrees with reactions (c) and (d).

Dehydrochlorination of (I) by equation (b) should have resulted in amine (IV), a compound that is already known. We established that the product of eliminating one hydrogen chloride molecule from amine (I) was not amine (IV). It seems to us, that all of this suggests that dehydrochlorination of (I) proceeds by equation (a) and leads to 1-dimethylamino-2-chlorobutene-2 (VI).

The reaction with alkalies was carried out at room temperature. The degree of dehydrochlorination was determined by the amount of ionic halogen formed. The data obtained are given in the table. As can be seen from the data in the table, the saturated amines (I) and (II), containing 1 or 2 chlorine atoms in the γ-position and a hydrogen atom in the β-position, dehydrochlorinated even at room temperature; thus amine (II) had as great a reaction rate as its methiodide (IIa). However, the picture changed sharply in the absence of a hydrogen atom in the β-position. Amine (III) did not dehydrochlorinate at all at room temperature, while at the same time all 4 chlorine atoms of its methiodide (IIIa) were almost completely changed into the ionic state after a 2-hour reaction with aqueous alkali. β,γ-Unsaturated amines with a chlorine atom in the γ-position and hydrogen in the β-position (IV), as well as with the reverse positions of these atoms (VI), were stable to alkali at room temperature.

(VI) was not dehydrochlorinated even when boiled on a water bath under conditions at which amine (IV) was dehydrochlorinated with the formation of dimethylaminobutine-2 [2]. Thus the position of the chlorine and hydrogen atoms being split off in amine (IV) was less stable than in amine (VI).

As regards the methiodides of these amines, it may be seen from the table data that their dehydrochlorination, although slow, still does proceed at room temperature; here the dehydrochlorination rate of (IVa) exceeds that of (VIa). The dehydrochlorination rate of (VIa) was determined by the data on the elimination of the second hydrogen chloride molecule from (Ia). Thus, in changing from the amine to the methiodide in all the given examples the elimination of hydrogen chloride was facilitated.

As can be seen from the table data, some of the methiodides, when treated with aqueous alkali, even at room temperature, were not only dehydrochlorinated but underwent deeper changes. Thus, for example, with (IIa), (IIIa) and (Va), even after standing for a short period with aqueous alkali, we could distinctly smell trimethylamine. Compound (IIa) lost a hydrogen chloride molecule and decomposed with the formation of trimethylamine and a polymer of 2,3-dichlorobutadiene-1,3. Compound (Va) did not undergo dehydrochlorination but also decomposed with the formation of trimethylamine and a polymer of 2,3-dichlorobutadiene-1,3. One may suppose from the similiarity of the final products of the reactions of (IIa) and (Va) with aqueous alkali that the reactions proceed according to the equation:

$$(CH_3)_3\overset{\overset{I}{|}}{N}-CH_2-CHCl-CCl_2-CH_3 \xrightarrow{NaOH} (CH_3)_3\overset{\overset{I}{|}}{N}-CH_2-CCl=CCl-CH_3 \xrightarrow{NaOH}$$

$$\rightarrow (CH_3)_3\overset{\overset{OH}{|}}{N}-CH_2-\overset{(IIa)}{CCl}=CCl-CH_3 \rightarrow (CH_3)_3N + CH_2=\overset{(Va)}{CCl}-CCl=CH_2 + H_2O.$$

This reaction may be accelerated by heating. The 2,3-dichlorobutadiene-1,2 was immediately distilled in quite good yield (75-80%). Thus, this reaction could be used as a laboratory method of preparing 2,3-dichlorobutadiene-1,2. The dehydrochlorination and decomposition of these salts may also be carried out with weaker bases. However, the reaction then proceeds much more slowly. Thus, for example, an aqueous solution of (IIa), when treated with triethylamine at room temperature was dehydrochlorinated in two days by only 74% (calculated on one HCl). The polymer of 2,3-dichlorobutadiene-1,3, however, precipitated only after prolonged standing. There was practically no alkaline decomposition of (IVa) and (VIa) at room temperature. Decomposition of (IVa)

Results of Reactions with Alkali at Room Temperature

Starting compound	Reaction time (in hours)	Amount of ionic halogen formed (in gram-atoms per mole of compound)	Products obtained	Remarks
(I) $(CH_3)_2N-CH_2-CHCl-CHCl-CH_3$	10	0.27	$(CH_3)_2N-CH_2-CCl=CH-CH_3$	—
(Ia) Methiodide	10	1.01	$(CH_3)_3N-CH_2-CCl=CH-CH_3$ I	Above 100° it is deomposed by aqueous alkali into trimethylamine and vinylacetyleme
	25	1.20		
(II) $(CH_3)_2N-CH_2-CHCl-CCl_2-CH_3$	4	0.886	$(CH_3)_2N-CH_2-CCl=CCl-CH_3$	Clear solution
	10	1.00		
(IIa) Methiodide	4	0.880	$(CH_3)_3N \cdot (CH_2-CCl=CCl-CH_2)_n$	A white polymer precipitated
	10	1.00		
(III) $(CH_3)_2N-CH_2-CCl_2-CCl_2-CH_3$	10	0.00	Starting compound unchanged	—
(IIIa) Methiodide	2	3.85	$(CH_3)_3N \cdot CH_3-C\equiv C-C(=O)-OH$	Clear solution
(IV) $(CH_3)_2N-CH_2-CH=CCl-CH_3$	10	0.00	Starting compound unchanged	It is dehydrochlorinated when heated for a long time with alcoholic alkali on a boiling water bath [2]
(IVa) Methiodide	10	0.21	$(CH_3)_3N-CH_2-C\equiv C-CH_3$ I	Above 60° it is deomposed by aqueous alkali into trimethylamine and a mixture of chloroprene and vinylacetylene.
(V) $(CH_3)_2N-CH_2-CCl=CCl-CH_3$	10	0.00	Starting compound unchanged	—
(Va) Methiodide	10	0.00	$(CH_3)_3N \cdot (CH_2-CCl=CCl-CH_2)_n$	A white polymer precipitated
(VI) $(CH_3)_2N-CH_2-CCl=CH-CH_3$	10	0.00	Starting compound unchanged	It is dehydrochlorinated by boiling for 12 hours with a 30% KOH solution in polyethylene glycol.

proceeded smoothly at the temperature of a boiling water bath and lead to the formation of trimethylamine and a mixture of vinylacetylene and chloroprene [3]. Under similiar conditions the dehydrochlorination product of (Ia) did not undergo noticeable decomposition, but at a temperature of 110° a vigorous reaction began with the formation of trimethylamine and vinylacetylene in almost theoretical yields. The temperature conditions of the reaction and the absence of chloroprene in the reaction products indicate that the dehydrochlorination of (Ia), preceding its decomposition, does not proceed through the stage of formation of the salt (IVa). Of course, there is the possibility that it does not occur either through the stage of formation of (VIa). This problem needs further clarification.

The dehydrochlorination-decomposition of (IIIa), which leads to the formation of trimethylamine and tetrolic acid, was described earlier [8]. In order to check the hypothesis that the tetrolic acid was formed according to scheme

$$(CH_3)_3\overset{I}{N}-CH_2-CCl_2-CCl_2-CH_3 \xrightarrow{NaOH} (CH_3)_3\overset{OH}{N}-C\equiv C-C\equiv CH \longrightarrow$$

$$(CH_3)_3N + \overset{(IIIa)}{[H-C\equiv C-C\equiv C-OH]} \longrightarrow [CH_2=C=C=C=O] \xrightarrow{NaOH}$$

$$\longrightarrow CH_3-C\equiv C-C\overset{O}{\underset{ONa}{<}}$$

i.e. through the stage of the formation of a base with a butadiinyl radical, we synthesized trimethyl-(α,β-dibromoethyl)-ammonium bromide, described by Bode [9], and subjected it to alkaline decomposition. By analogy, one would expect the formation of acetic acid.

$$(CH_3)_3\overset{Br}{N}-CHBr-CH_2Br \xrightarrow{NaOH} (CH_3)_3\overset{OH}{N}-C\equiv CH \longrightarrow (CH_3)_3N +$$

$$+ [H-C\equiv C-OH] \longrightarrow CH_2=C=O \xrightarrow{NaOH} CH_3-\overset{O}{\overset{\|}{C}}-ONa$$

Actually, acetic acid was isolated from the aqueous layer after acidification and was identified by its smell and silver salt analysis.

EXPERIMENTAL

1-Dimethylamino-2,3-dichlorobutane. Chlorine was passed through a solution of 49.5 g of 1-dimethylaminobutene-2 in 60 ml of concentrated hydrochloric acid until the theoretical amount had been absorbed. By working up in the usual way we obtained 59.8 g (70%) of material.

B. p. 89-90° (32 mm), d_4^{20} 1.0722, n_D^{20} 1.4589, MR_D 43.44. M 170.9. $C_6H_{13}NCl_2$. Calculated: MR_D 43.58. M 170.

The methiodide had m.p. 204-205° (from alcohol).

Found %: I 40.54. $C_7H_{16}NCl_2I$ Calculated %: I 40.70.

Treatment of trimethyl-(polychloroalkyl)-ammonium iodide with aqueous alkali. A solution of 0.005 mole of the quaternary salt being examined, 2 g of sodium hydroxide and 20 ml of water was left to stand at room temperature. Then the amount of ionic halogen was determined by precipitation with silver nitrate. The amount of ionic halogen formed expressed as gram-atoms per mole of compound are given in the table. In experiments with salts (IIa) and (Va), a pure white polymer precipitated.

Found %: Cl 57.05 (IIa) and 57.35 (Va). $C_4H_4Cl_2$. Calculated %: Cl 57.72.

The amine was extracted from the aqueous layer with ether. In all cases we obtained the same amine, whose picrate melted at 216°, which corresponded to trimethylamine.

Treatment of dimethyl-polychloroalkylamines with alkali. This was performed as above, with the one difference that methyl alcohol was used as the solvent. The results obtained are given in the table.

2,3-Dichlorobutadiene-1,3. A solution of 12 g of sodium hydroxide in 30 ml of water was gradually added to 34.6 g of trimethyl-(2,3,3-trichlorobutyl)-ammonium iodide, heated on a water bath. The products of the dehydrochlorination – decomposition reaction and water vapor readily began to distil off. The distillate was acidified and extracted with ether. We obtained 9.1 g (74%) of a readly polymerizable substance.

B.p. 90-93° (680 mm), d_4^{20} 1.1872, n_D^{20} 1.4872, MR_D 29.79. $C_4H_4Cl_2$. Calculated 29.46 [10].

From the reaction flask we recovered 2 g of a polymerized material.

Alkaline decomposition of trimethyl-(2,3-dichlorobutyl)-ammonium iodide. A solution of 31.2 g (0.1 mole) of salt (Ia) and 22.4 g of potassium hydroxide in 60 ml of water was heated on a sand bath. Decomposition began with the reaction mixture at 110°. After passing through washers with water and titrating acid, the gases coming off entered a gasometer. We found 0.090 g of amine; the hydrochloride melted at 271-272°, which corresponds to the melting point of trimethylamine hydrochloride. In the gasometer we collected about 2 liters of vinylacetylene, which gave a characteristic yellow precipitate with Ilosvaya's solution. Chloroprene was not found in the reaction products.

Dehydrochlorination of 1-dimethylamino-2,3-dichlorobutane. A solution of 34 g (0.2 mole) of amine (I) and 14 g of potassium hydroxide in 80 ml of methyl alcohol was heated for 1 hour on a boiling water bath. 13 g (87%) of potassium chloride precipitated. After distilling off the methyl alcohol and distilling the residue 3 times; we obtained the following fractions: 1st 134-135°, 6.9g, 2nd 135-140°, 4.7 g; 3rd 140-150°, 3.7 g; 4th 150-165°, 4.2 g. By titration of these fractions, we found molecular weights of 137, 133, 130 and 158 respectively. The last fraction contained a little of the original amine.

For 1st fraction we found d_4^{20} 0.9322, n_D^{20} 1.4455, MR_D 38.09; Calc. 38.24.

Found %: N 10.80. M 137. $C_6H_{12}NCl$. Calculated %: N 10.48. M 133.5.

We obtained a picrate with m.p. 127-128°. When mixed with the picrate of 1-dimethylamino-3-chlorobutene-2, which has m.p. 118-119°, the melting point was depressed.

Trimethyl-(2-chloroethyl)-ammonium chloride. Trimethylamine was passed through dichloroethane at 50-65° for 8 hours. 23.6 g of trimethylamine was absorbed. After two days, the crystals, which precipitated were filtered off and washed with ether, m.p. 240° [11]. The yield was 50.6 g (80%).

Found %: Cl' 22.22. $C_5H_{13}Cl_2N$. Calculated %: Cl' 22.46.

Trimethyl-(1,2-dibromoethyl)-ammonium bromide. 0.25 mole of an alcohol solution of potassium hydroxide was added to a solution of 39.5 g (0.25 mole) of trimethyl-(2-chloroethyl)-ammonium chloride in 60 ml of methyl alcohol. 16.8 g (90.3%) of potassium chloride precipitated. The filtrate was saturated with hydrogen bromide and 60 g of bromine in 100 ml of alcohol was added. After evaporating off the solvent, the residue crystallized. After recrystallization from alcohol, it melted at 165° [9]. The yield was 65 g (90.6%).

Found %: Br' 24.87. $C_5H_{12}Br_2N$. Calculated %: Br' 24.54.

Formation of acetic acid by alkaline decomposition of trimethyl-(1,2-dibromoethyl)-ammonium bromide. A solution of 9.78 g of trimethyl-(1,2-dibromoethyl)-ammonium bromide and 7 g of potassium hydroxide in 50 ml of water was heated first on a water bath and then on a sand bath. The trimethylamine evolved was trapped with titrating acid. We found 0.021 mole of amine (70%). The residue in the distillation flask was acidified and distilled. The smell of acetic acid was detected. A small amount of the distillate was heated with silver oxide. The filtrate was evaporated down to give crystals of silver acetate.

Found %: Ag 64.73. $C_2H_3O_2Ag$. Calculated %: Ag 64.68.

SUMMARY

New data were obtained confirming the accuracy of the observation made earlier that in going from an amine, containing a haloalkyl, to its quaternary salt, the elimination of hydrogen halide was facilitated. It was established that dehydrochlorination of amines to form β,γ-multiple bonds from chlorine in the γ-position and hydrogen in the β-position proceeds more readily than with them in the reverse positions. It was shown that decomposition of trimethyl-(2,3-dichlorobuten-2-yl)-ammonium and trimethyl-(2,3,3-trichlorobutyl)-ammonium with aqueous alkali, occurred even at room temperature and lead to the formation of 2,3-dichlorobutadiene-1,3. It

was shown that the decomposition of trimethyl-(α,β-dibromoethyl)-ammonium bromide with aqueous alkali lead to the formation of trimethylamine and acetic acid. 1-Dimethylamino-2,3-dichlorobutane and 1-dimethylamino--2-chlorobutene-2 were prepared and described for the first time.

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ALKYLATION OF NAPHTHALENE WITH NORMAL ALCOHOLS IN THE PRESENCE OF BF_3

I. A. Romadan

Many papers have been published in recent years on the preparation and investigation of alkylnaphthalenes and alkyldiphenyls as model hydrocarbons [1-13]. These compounds are found in petroleum products and, together with other aromatic hydrocarbons, impart valuable qualities to them. Many alkylnaphthalenes and diphenyls find application, for example, in the preparation of sulfo derivatives – emulsifiers and detergents [14], and as oils for diffusion pumps [15-17].

Alkylnaphthalenes, prepared by direct alkylation with olefins and alkyl halides in the presence of various catalysts, have been investigated by many chemists, while there have been comparatively few papers published on those prepared with alcohols. Direct alkylation in the presence of $AlCl_3$, $ZnCl_2$, H_2SO_4, BF_3 and other catalysts gives a complex mixture of difficultly separable substances which makes their investigation difficult.

In this work we carried out the alkylation of naphthalene with n-propyl, n-butyl, n-amyl and n-hexyl alcohols in the presence of BF_3 at normal pressure and a temperature of 165-170°. As a result we obtained good yields of mono- and dialkylnaphthalenes. Their refractive indices, specific gravities as well as other constants agree in many cases with the data for α- and β-alkylnaphthalenes prepared by synthetic methods [8]. The yield of dialkylnaphthalenes increases with an increase in the molecular weight of the starting alcohols. Thus, in the case of the reaction with n-hexyl alcohol, the yield of 1,4-dihexylnaphthalene was 38-40%, while in alkylation with n-propyl alcohol the amount of dipropylnapthalenes was not more than 12-18%. The overall yield of mono- and dialkylnapthalenes was 88-98%, calculated on the starting naphthalene.

Alkylation with normal alcohols gave substances containing only normal radicals, which was confirmed by special experiments on the deuterium exchange of hydrogen in the naphthalene rings and in the radical in the position α to the naphthyl. No formation of olefin polymers was observed in any of the experiments. The reaction time with normal alcohols was 2-3 times greater than with alcohols with isomerized radicals. These facts seem to indicate that condensation rather than alkylation occurred with normal alcohols; however, this requires further proof.

EXPERIMENTAL

For the preparation of the molecular compounds, we used alcohols with the following data:

n-propyl – b.p. 97-98°, n_D^{20} 1.3824, d_4^{20} 0.8030; n-butyl – b.p. 117-118°, n_D^{20} 1.3908, d_4^{20} 0.8091; n-amyl – b.p. 139° (764 mm), n_D^{20} 1.4109; n-hexyl – b.p. 156-157°, n_D^{20} 1.4136.

The alcohols were slowly saturated with BF_3 while cooled in ice, by the method developed previously [18]; thus we obtained compounds corresponding to the formula $2ROH \cdot BF_3$. Alkylation was carried out in a round-bottomed flask, fitted with a mechanical stirrer and a reflux condenser, in which was placed 1 mole of naphthalene, which had been recrystallized from methyl alcohol. 1.5 moles of the molecular compound (calculated on the alcohol) was added dropwise to the naphthalene, which was heated to 165° and stirred vigorously. The BF_3 thus evolved was absorbed in a wash bottle with anhydrous, cooled alcohol. Under the given conditions, we succeeded in regenerating 70-75% of the BF_3. During the addition of the molecular compound, the temperature was always kept at 165-170°. After introducing the reagent, the reaction mixture was heated for a further 4-6 hours with stirring. The oily upper layer was separated and steam distilled to remove unreacted naphthalene. The oil

Alkylation of Naphthalene with Normal Alcohols

Experiment No.	Name	Boiling point	n_D^{20}	d_4^{20}	Solidification point	Yield calculated on the alkylnaphthalenes	M	
							Found	Calculated
1	1-n-Propylnaphthalene	273°, 67.3° (0.2 mm)	1.5919	0.9903	−15°	42	171.4	170
	2-n-Propylnaphthalene	274.7, 82.2 (0.57 mm)	1.5874	0.9773	−4	40	170.3	170
	Di-n-propylnaphthalene	282, 102.5 (0.3 mm)	1.5723	0.9501	—	18	211	212
2	1-n-Butylnaphthalene	289, 84.5 (0.1 mm)	1.5809	0.9773	−24	44	186	184
	2-n-Butylnaphthalene	292, 87.3 (0.1 mm)	1.5778	0.9651	−6	35	183	184
	1,4-Di-n-butylnaphthalene	321, 107 (0.1 mm)	1.5557	0.9419	−29	21	238	240
3	1-n-Amylnaphthalene	304, 87.1 (0.2 mm)	1.5731	0.9668	—	—	195	198
	2-n-Amylnaphthalene	308, 99.9 (0.2 mm)	1.5704	0.9571	—	—	196	128
4	1-n-Hexylanphthalene	320, 104.7 (0.1 mm)	1.5650	0.9576	−21°	42	209	212
	2-n-Hexylnaphthalene	323, 108.5 (0.1 mm)	1.5622	0.9491	−7	18	210.7	212
	Di-n-Hexynaphthalene	347, 155 (2.0 mm)	1.5391	0.9207	−27	40	288	296

Footnote. Yield calculated on the starting naphthalene (in %): for experiment No. 1 – 88, for experiment No. 2 – 93 and for experiment No. 3 – 98.

was dried and again distilled over metallic sodium and then on a vacuum column with an efficiency of 48-50 theoretical plates.

By the alkylation of naphthalene with n-propyl alcohol, we obtained a mixture of 1- and 2-n-propylnaphthalenes, which was confirmed by means of ultraviolet spectra. If this substance was dissolved in ether and the test tube placed in a mixture of solid carbon dioxide and acetone (a temperature of -30°), then the 2-n-propylnaphthalene crystallized. After the separation, we were able to obtain α- and β-n-propylnaphthalenes, giving characteristic lines in the ultraviolet region of the spectrum. The constants corresponded to the literature data. We obtained 1,4-di-n--propylnaphthalene, which was oxidized to give 0.45 g of 1,4-naphthalenedicarboxylic acid with m.p. 301° [19].

In the reaction with n-butyl alcohol, the 1- and 2-n-butylnaphthalenes were isolated directly by distillation on a column (see exp. 2 in the table). The 1,4-di-n-butylnaphthalene obtained was also oxidized. The substance is not described in the literature.

For the preparation of n-amylnaphthalenes, n-amyl alcohol was prepared by hydrolysis of amyl iodide. We isolated only 1- and 2-n-amylnaphthalenes as a result of a small amount of starting alcohol.

With n-hexyl alcohol, we obtained mono- and dihexylnaphthalenes in 98% yield calculated on the naphthalene. Of these, the monoformed 60% and the di-40%. Of the mono-, the main part was 1-n-hexylnaphthalene (61--66%, calculated on the monohexylnaphthalenes). We obtained a new substance, 1,4--di-n-hexylnaphthalene – a viscous oil, which was not decomposed on distillation over metallic sodium at 347°, and was stable to oxidants. All the results of the investigation are given in the table.

In alkylating naphthalene with normal alcohols, we obtained dialkylnaphthalenes as colorless, comparatively viscous substances with the following analytical data.

1. 1,4-Di-n-propylnaphthalene; Found %: C 90.29; H 9.59. $C_{16}H_{20}$. Calculated %: C 90.14; H 9.86.

2. 1,4-Di-n-butylnaphthalene; Found %: C 90.11; H 9.90. $C_{16}H_{24}$. Calculated %: C 89.97; H 10.03.

3. Di-n-hexylnaphthalene: Found %: C 88.96; H 11.14. $C_{22}H_{32}$. Calculated %: C 89.12; H 10.88.

SUMMARY

1. A method has been developed for alkylating naphthalene with molecular compounds of normal alcohols and BF_3 and for preparing alkylnaphthalenes in 88-98% yields.

2. A mixture of 1- and 2-n-alkylnaphthalenes in almost equal amounts was obtained from lower alcohols at normal pressure and a temperature of 165-170°. As the molecular weight of the starting alcohols increased the amount of 1-alkylnaphthalene increased and, at the same time, the yield of di-alkylnaphthalenes rose.

3. We isolated 1,4-di-n-alkylnaphthalenes, which have not been described in the literature.

4. All the substances obtained were oily, colorless liquids, which did not decompose on distillation at normal pressure and were extremely stable to oxidants.

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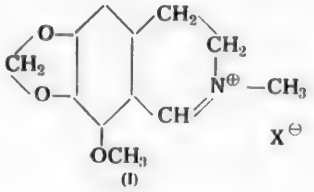
STRUCTURAL PROBLEMS OF COTARNINE DERIVATIVES

I. REACTIONS OF COTARNINE WITH SODIUM BISULFITE AND SULFUROUS ACID

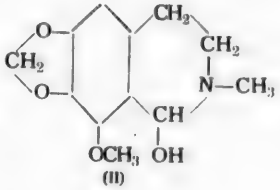
Denesh Beke and Marietta Martosh-Bartsai

Cotarnine, obtained by the oxidative degradation of narcotine, is used in medicine in the form of various salts. As it has some of the characteristics of a pseudobase, cotarnine is of interest from the theoretical point of view. The structure of cotarnine and its derivatives has been the subject of a number of papers, but, up to now, has not been definitely established.

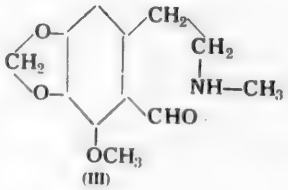
In an acid medium, cotarnine is present as a quaternary ammonium ion (I), while in an alkaline medium it exists as an un-ionized pseudobase or aminocarbinol (II), feebly soluble in water.



(I)



(II)



(III)

The aminocarbinol form is also present in nonpolar solvents; in solution in water or other polar solvents, it has been shown by a number of investigators [1-3] that there is a dynamic equilibrium between the aminocarbinol and quaternary ammonium hydroxide, which is displaced in the direction of the ammonium base on dilution, and in the direction of the aminocarbinol on the addition of hydroxyl ions.

Some chemical reactions of cotarnine have been interpreted [4] on the basis of a third structure, consisting of the opened aminoaldehyde form (III).

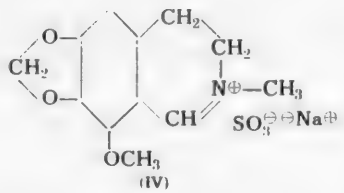
On acetylation cotarnine gives an N-acetyl derivative; alkylation gives a quaternary ammonium salt, which suggests the presence of a secondary amino group, and this can only be present in the aminoaldehyde form. In addition, cotarnine gives condensation products with various nucleophilic reagents (containing amino or active methylene groups), with which aldehydes react with elimination of water. Although the existence of structure (III) cannot be established spectroscopically, it may be supposed that the aminocarbinol and aminoaldehyde forms exist together in tautomeric equilibrium (ring–open chain tautomerism) in which the aminocarbinol form predominates. Under the influence of various reagents the equilibrium may be displaced in the direction of the aminoaldehyde form. It may also be supposed that cotarnine exists only in the cyclic form (this is supported by spectroscopic evidence), and that the above-mentioned reagents can interact with this, giving derivatives of the aminoaldehyde form [5].

Different derivatives of cotarnine may also exist in cyclic or open-chain forms; some of them have hitherto been described as derivatives of the aminoaldehyde form of cotarnine, while, with others, no preference has been established for any of the forms in dynamic equilibrium.

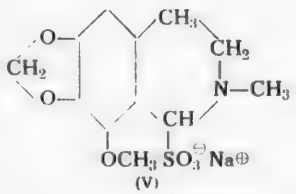
In the present investigation we have investigated reactions of cotarnine and its derivatives from which, either from the course of the reaction, or from the structure of the products, it should be possible to draw conclusions as to the existence of the aminoaldehyde form. For instance, in connection with work on the purifica-

tion of crude cotarnine, we have investigated the effects of adding sodium bisulfite and sulfurous acid, about which there is no information in the literature.

As we reported previously to the conference on organic chemistry in September 1953 at Debreczen [6], cotarnine dissolves in an aqueous solution of an equivalent amount of sodium bisulfite to give an orange-yellow solution, and, only after standing for several days, or on adding excess of solid sodium bisulfite, pale yellow crystalline needles are formed, which are soluble in water only after prolonged shaking or stirring. Analysis showed that this compound was formed by the elimination of one molecule of water from cotarnine and sodium bisulfite; consequently it is not a derivative of the aminoaldehyde form, but a condensation product. So, since cotarnine reacts in acid media in its quaternary ammonium form, and since sodium bisulfite has an acid reaction, it is natural to suggest that the initial product is the quaternary ammonium salt (IV), readily soluble in water. The slow crystallization and the slow rate of solution of the crystals in water suggest that there is a reversible isomerization, analogous to that which has been established between the quaternary ammonium and aminocarbino forms of cotarnine, or between cotarnine cyanide and 1-cyanohydrocotarnine. We have assigned the structure of the sodium dalt of hydrocotarnine-1-sulphonic acid (V) to the crystals.



(IV)



(V)

An attempt was made to demonstrate the supposed isomeric transformation by measurement of conductivity; but the mixed solutions of cotarnine chloride with its equivalent of sodium bisulfite did not show any change in conductivity with time at constant temperature. From this it may be concluded that, in solution, the equilibrium is completely toward the side of the quaternary ammonium salt.

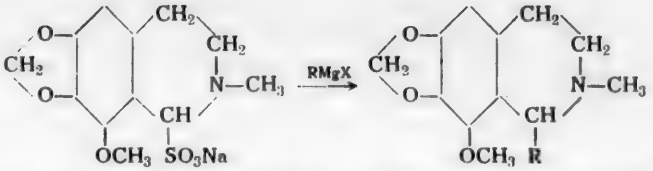
When sulphur dioxide was passed through a supension of cotarnine in water, the latter first dissolved and then gave a crystalline compound, which dissolved with difficulty, and was probably the free hydrocotarnine-1--sulphonic acid, corresponding to the above sodium salt.

Our hypothesis was completely confirmed by spectroscopic investigations in the infrared and ultraviolet regions. The infrared spectra (in liquid paraffin) of the crystalline sodium bisulfite and sulfur dioxide compounds agreed precisely with that of 1-cyanohydrocotarnine, and were quite different from that of cotarnine chloride (see Fig.). Consequently the crystalline compounds are essentially derivatives of hydrocotarnine, substituted in the 1 position.

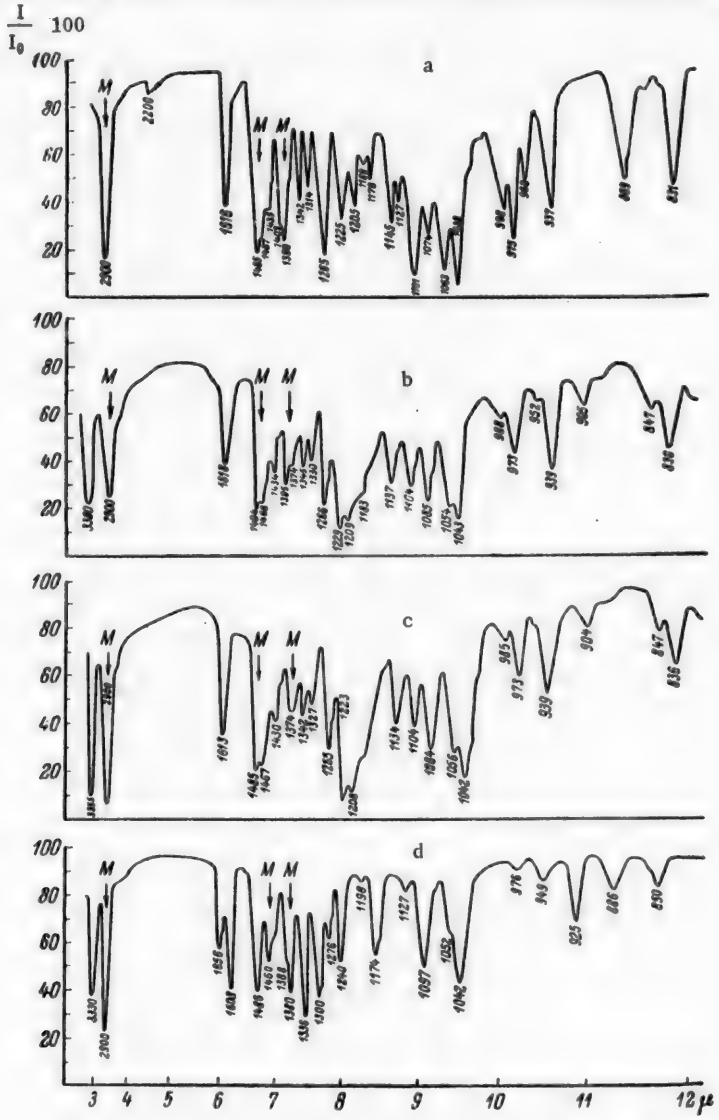
In dilute aqueous solution (1.5 mg/100 ml) the ultraviolet spectra of all four substances are of a single type, identical with Skinner's [3] curve D, which shows that, at this high dilution, all the substances exist in the form of quaternary salts of dihydro-isoquinoline. The slow change from the crystalline to the dissolved state, and vice versa, is probably connected with the supposed isomeric transformation; on the other hand, their formation accords well with the cyclic structure of cotarnine and does not agree with the hypothesis of the aminoaldehyde form.

Under the action of dilute alkali, both hydrocotarnine-1-sulfonic acid and its sodium salt decompose into cotarnine and the sulfite of the alkali metal. The conversion of crude cotarnine, obtained by the oxidation of narcotine, into a well crystallized and easily purifiable compound, and subsequent regeneration under the influence of alkali, gives a convenient and economical method for the purification of crude cotarnine [7, 8], as compared with methods described in the literature [9, 10], which either involve a great loss of cotarnine or are very complicated and usuited to industrial practice. The above compounds are also suitable for the prolonged storage of cotarnine, since they are less subject to oxidation than free cotarnine, which can easily be regenerated from them.

Both the free sulfonic acid and its sodium salt can be converted into 1-alkyl or 1-aryl derivatives by the action of Grignard reagents, with an almost theoretical yield:



Freund and Reitz [11, 12] obtained compounds of this type by the action of Grignard reagents on cotarnine, cotarnine chloride or 1-cyanohydrocotarnine. But, with cotarnine, the yield is very small since it is poorly soluble in ether, and the greater part remains unchanged or is converted into other products. Better yields are obtained with cotarnine chloride or 1-cyanohydrocotarnine, but the preparation of the starting materials requires a special operation; while with 1-cyanohydrocotarnine there is the known hazard due to the evolution of hydrocyanic acid on reaction with the Grignard reagent. 1-Alkyl- and 1-aryl derivatives of hydrocotarnine can be used as intermediates for the synthesis of isoquinoline derivative which are active pharmocologically.



Spectroscopic Investigation of Substances in the Infrared Region.
a) 1-cyanohydrocotarnine; b) hydrocotarnine-1-sulfonic acid; c) sodium salt of hydrocotarnine-1-sulfonic acid; d) cotarnine chloride.

EXPERIMENTAL

Sodium salt of hydrocotarnine-1-sulfonic acid (V). Cotarnine (2.37 g) was added with vigorous shaking to a solution of 11 g of sodium bisulfite in 20 ml of water. Most of the cotarnine dissolved to give an orange solution, and then the whole, including the undissolved part, was converted to crystals of a quite different shape, as was clearly visible on the glass. On heating to boiling, the crystals went into solution, but appeared again on cooling in the form of bunches of radial crystals. After separation, washing with a small quantity of ice cold distilled water and drying in air, there was obtained 2.9 g (96%) of pale yellow crystals in the form of needles.

Found %: N 4.42; S 10.07. $C_{12}H_{14}O_6NSNa$. Calculated %: N 4.33; S 9.92.

Measurement of conductivity. Measurements were made with a Wheatstone bridge and a 5 decade resistance, with automatically compensated leads. The cell constant was 0.36.

The observed resistance, for mixtures of equal volumes of 0.01 M cotarnine chloride and 0.01 M sodium bisulfite at 0°, are shown in the following table.

Time (min)	Resistance (Ω)
0	489
5	500
10	501
30	507
60	503
120	502
180	503
24 hours	507

The observed variations are within the limits of experimental error.

Hydrocotarnine-1-sulfonic acid. Cotarnine (2.37 g) was suspended in 10 ml of water and agitated while a vigorous stream of SO_2 was passed through. The cotarnine dissolved at first, but pale yellow crystals began to form as the passage of SO_2 was continued. The next day the crystals were separated, washed with ice water and dried in air. The product obtained contained one molecule of water of crystallization, which was readily lost at temperatures above 50°. The yield was 2.65 g (83%). A better yield (88%) was obtained if the cotarnine was dissolved in a solution of an equivalent quantity of sodium bisulfite, and sulphur dioxide was then passed through this solution.

Found %: C 45.13; H 5.31; S 10.16; H_2O 5.72. $C_{12}H_{15}O_6NS \cdot H_2O$. Calculated %: C 45.15; H 5.32; S 10.03; H_2O 5.63.

Purification of crude cotarnine. Crude cotarnine (23.7 g), obtained by the oxidation of narcotine with nitric acid, was dissolved in a cold solution of 12 g of $NaHSO_3$ in 200 ml of water. With vigorous stirring, 118 g of solid $NaHSO_3$ was added to the solution, whereupon the sodium salt of hydrocotarnine-1-sulphonic acid crystallized out. The next day the crystals were separated and dissolved in 480 ml of water by stirring and gentle warming (to 30°). The cold solution was maintained at 0 to 2°, and a solution of 16 g of chemically pure caustic soda in 50 ml of water was added, drop by drop, with stirring and scraping of the glass walls. The formation of the powdery precipitate was complete after 2 hours in a refrigerator, and the powder was then separated, washed well with a small quantity of ice cold distilled water and dried in air or in a vacuum desiccator. The yield was 21.5 g (91% of the crude cotarnine). The principle of cotarnine is light yellow in color, m.p. 132° (decomp.). A 92% yield of pure cotarnine was obtained from 12 kg of narcotine by oxidation and purification of the crude product as above.

Preparation of Hydrocotarnine Derivatives, Substituted in the 1 Position

a) Finely ground hydrocotarnine-1-sulfonic acid (3.01 g) was added, in small portions with stirring, to a Grignard solution, prepared from 10.8 g of ethyl bromide, 2.5 g of magnesium and 80 ml of dry ether, and the solution was then boiled gently for 1 hour. After cooling and decomposing the product with a solution of ammonium chloride, the aqueous layer was extracted a few times with ether, the combined ether extracts were dried over anhydrous $CaCl_2$ and the ether was evaporated off. There remained a yellow oil which quickly crystallized. Recrystallization from aqueous alcohol gave 2.35 g (94.5%) of 1-ethylhydrocotarnine of m.p. 59°, which showed no depression of melting point when mixed with the product obtained by the method of Freund and Reitz [12].

1-Methylhydrocotarnine (yield 91%) and 1-isopropylhydrocotarnine (yield 87%) were prepared in a similar manner, using methyl and isopropyl iodides. As these products are liquid at room temperature, the hydriodides, which crystallize well, were used to identify them with products obtained by the method of Freund and Reitz [12].

b) The addition of 3.23 g of the sodium salt of hydrocotarnine-1-sulfonic acid to a Grignard solution of 10.4 g of bromobenzene and 2.5 g of magnesium in 80 ml of dry ether, and working up as described under a), gave 2.9 g (97.5%) of 1-phenylhydrocotarnine, with an m.p. of 97°, which showed no depression of melting point when mixed with the product obtained by the method of Freund and Reitz [12].

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SUMMARY

1. The previously unkown sodiumsalt of hydrocotarnine-1-sulfonic acid and the corresponding free sulfonic acid have been obtained as well crystallized products by the action of sodium bisulfite and sulfur dioxide on cotarnine. Their structures have been established spectroscopically. Their ultraviolet spectra show that, in dilute aqueous solution, they exist in the form of quaternary salts of dihydroisoquinoline.

2. Under the influence of dilute alkali they decompose to form cotarnine and the sulfite of the alkali metal, and hence are particularly useful for the purification and storage of crude cotarnine.

3. They react with Grignard reagents to give excellent yields of hydrocotarnine derivatives substituted in the 1 position.

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INVESTIGATIONS IN THE SPHERE OF COMPOUNDS LABELED WITH C^{14} AND N^{15}

COMMUNICATION IV. A NEW METHOD OF INVESTIGATING DUAL REACTIVITY AND TAUTOMERISM

I. INVESTIGATION OF TRIAZINE (DIAZOAMINE) SYSTEMS

M. M. Shemyakin, V. I. Maitind and E. Gomes

Dual (multiple) reactivity of a substance is usually explained as the result of tautomeric transformation, but recently it has received a new interpretation in the work of A. N. Nesmeyanov and M. I. Kabachik (see "The Complex State" [1]). These investigators suggest that dual (multiple) reactivity can not only be caused by tautomeric transformations, but also by a process of transfer of the reactive center at the time of the reaction. This view is now sufficiently well-founded for its further discussion to be superfluous. But the application of these ideas to individual concrete examples is a complicated matter, since it is at present difficult to predict which substances are capable of tautomeric change, and under what conditions, and in which substances the transfer of a reactive center can occur. In each case it is necessary to investigate the cause of dual reactivity by experiment, carefully demonstrating the presence or absence of a second tautomeric form. Here it must be realized that, not only processes leading to the transfer of a reactive center, but tautomeric transformations may often only occur as the result of the influence of reagents and the conditions of the reaction. So that, if particular reagents under a definite set of conditions yield derivatives corresponding to two forms of a substance, it is still necessary to demonstrate the presence or absence of the second tautomeric form under these or similar conditions.* Sometimes insufficient attention is paid to this point, and dual reactivity is attributed to transfer of a reactive center without strict proof that there is no second tautomeric form. The problem is specially difficult when the tautomeric equilibrium is strongly displaced to one side, since it is necessary to use very sensitive analytical methods to demonstrate the absence or presence of one tautomeric form at concentrations of the order 10^{-6} - 10^{-8} moles per liter [1]. For these conditions many methods of analysis require special precautions or become unreliable (e.g. spectroscopic methods). So that only in a very few cases (e.g. [2]) has it hitherto been possible to give a rigid proof that dual reactivity was due to the transfer of an active center and not to tautomeric transformation.

In order to extend the limited range of methods available for investigating this problem we considered the use of labelled compounds. This led to the proposal** of a new method, with which it should be possible, in a number of cases, to establish definitely whether dual reactivity was due to tautomerism or to transfer of a reactive center. The principle of this method, which is applicable to symmetric molecules containing systems of the type A= B – AX (where B may be the same as or different from A)***, is as follows: one of the terminal A atoms of the compound under investigation is labeled with the corresponding isotope, this labeled compound is then used to perform all the different types of reaction (not less than 3-4) which illustrate the dual reactivity, and, finally, the isotopic composition of the products is determined for each terminal A atom. In the case of tautomers, it is obvious that the isotopic compositions of the two terminal A atoms must always be the same after any reactions, since the ionotropic transformations in a perfectly symmetrical system will always be exactly equal for both A atoms. But with transfer of a reactive center (or direct substitution of the X atom by a bimolecular mechanism) the isotopic

* Unless, of course, this form was revealed under milder conditions.

** Contribution of M. M. Shemyakin to the All-Union conference on chemical kinetics and reactivity, held in Moscow June 20-24, 1955.

*** For example: $-N=N-NH-$, $-N=\underset{|}{C}-NH-$, $\rangle C=N-CH\langle$, $\rangle C=\underset{|}{C}-CH\langle$

compositions of the terminal A atoms after reaction will always be different; this difference will depend on the nature of the reagents and the conditions of the reaction and arises from the difference in reactivity of the two A atoms, one of which is linked to the X atom, and the other of which is not.

The proposed method can be used for investigating either the cause of dual reactivity in different types of compound or tautomeric transformations. It can be applied to a range of systems to investigate the mobility of tautomeric forms, and also to the mildest conditions in which tautomeric transformations can occur. It may be noted that this method has a number of advantages in principle over earlier methods.* Firstly, since it is based on the determination of the compositions of the terminal atoms of the tautomeric system and not on the concentrations of the tautomeric forms or their products, it is considerably more sensitive. Secondly, for the same reason, the new method makes it possible to use chemical methods of investigation without the danger that they will distort the true picture (this danger was never quite absent with most of the previous methods). Thirdly, the cause of dual reactivity can be investigated directly at the instant of reaction, and not merely under similar conditions, as in most earlier investigations. Finally, for the first time, symmetrically substituted systems of the type described can be investigated, since the necessary asymmetry is provided by isotopic substitution (previously, to distinguish the tautomers from each other, time was required to introduce substituents; this undoubtedly affected their mobility and position of equilibrium).

The method described has been used to investigate the triazine (diazoamine) system -N=N-NH-. Substances containing this grouping can form two classes of product, but themselves exist in only one form, which has been established for a large number of asymmetrically substituted triazines of the general type $R_1N{=}N{-}NHR_2$ by subjecting them to different transformations [4-7]. However these investigations did not reveal the structure of the triazines (the position of the triazine hydrogen atom) nor the cause of their dual reactivity – the absence or presence of transfer of an active center or tautomerism. And nothing was discovered about the degree of mobility of the system (the opinion was expressed that it was small [4]) nor the effect on it of different factors (surroundings, catalysts, reagents).

To answer these questions, our basic object was to investigate a simple aromatic triazine–diazoaminobenzene with one terminal nitrogen atom labeled with N^{15}, and, as a control, diazoaminobenzene with the central nitrogen atom similarly labeled For the synthesis of the first of these substances phthalimide-N^{15} was converted via anthranilic acid-N^{15} to aniline-N^{15}, and this was added rapidly to a buffered (pH 4.4-7.6) diazo solution prepared from unlabeled aniline and sodium nitrate. The product was pure enough to require only one or two recrystallizations. The 2-N^{15}-diazoaminobenzene was prepared similarly, starting with the labeled compound $NaN^{15}O_2$ [8].

In accordance with the requirements of the method, diazoaminobenzene, labelled at one of the terminal atoms, was subjected to a series of reactions which should show its dual reactivity. The reactions chosen differed in their conditions and nature, and in their influence on tautomeric transformations – one might strongly promote such transformations, another would practically exclude them. In the first class of reactions are the isomerization of diazoaminobenzene to aminoazobenzene (scheme 1), done without heating in the presence of acetic acid [10], and the decomposition of diazoaminobenzene to nitrogen and aniline (scheme 2), on heating with hydrochloric acid [11]. In the class which do not promote tautomerism are the thermal decomposition of solid diazoaminobenzene with elimination of nitrogen [12], and conversion to the corresponding acyl derivative by reaction with diphenylketene in the presence of anhydrous petroleum and diethyl ether [13] (schemes 2 and 3).

$$C_6H_5N{=}N{-}NHC_6H_5 \xrightarrow{CH_3COOH} C_6H_5N{=}NC_6H_4NH_2 \quad (1)$$

$$C_6H_5N{=}N{-}NHC_6H_5 \xrightarrow{HCl} C_6H_5NH_2 + N_2 \quad (2)$$

$$C_6H_5N{=}N{-}NHC_6H_5 \xrightarrow{(C_6H_5)_2CCO} C_6H_5N{=}N{-}NC_6H_5 \quad (3)$$

$$(C_6H_5)_2CHCO$$

The isomerization reaction according to scheme 1 was investigated with aminoazobenzene labelled at one of the terminal nitrogen atoms, and, as a control, with 2-N^{15}-diazoaminobenzene. In both cases the amino group

* Particularly the so-called methods of symmetry, cleavage and substitution; for details of these see Reference [3].

in the aminoazobenzene obtained was diazotized, the resulting diazo compound was decomposed in the presence of hydroquinone [14], and the resulting N_2 was analyzed isotopically with a mass-spectrometer. It was found that the N_2, obtained from diazoaminobenzene labeled at one of the terminal nitrogen atoms, had 25% of the initial concentration of isotope, while that from the 2-N^{15}-diazoaminobenzene contained none of the isotope. It thus appears that the nitrogen isotope is shared between the two terminal nitrogen atoms of the diazoaminobenzene, so that each contains 50% of the initial labeling. Precisely the same results were obtained when diazoaminobenzene, labeled at one of the terminal nitrogen atoms, was decomposed to give N_2 and aniline (scheme 2). This decomposition was carried out both by heating with hydrochloric acid and purely thermally. The N_2 evolved was immediately analyzed isotopically, and the aniline obtained was converted to a diazocompound, which was decomposed in the presence of cuprous chloride [14] to give N_2. In all cases the N_2 obtained contained 25% of the initial concentration of isotope, showing that the isotopic composition of both terminal nitrogen atoms of the diazoaminobenzene must have been the same.

The same picture emerged from the reaction of diazoaminobenzene, labeled at one of the terminal nitrogen atoms, with diphenylketene (scheme 3). The acyl derivative obtained was decomposed (by heating with alcohol, or acetic acid, or purely thermally) into N_2 and diphenylacetanilide, and the latter was hydrolyzed to aniline and converted to a diazo compound, which was decomposed to give N_2. The samples of N_2 all contained 25% of the initial concentration of isotope, showing that in this case, also, the isotopic compositions of the terminal nitrogen atoms of the diazoaminobenzene were the same.

Finally, it should be noted that the results obtained were independent of the pH (within the limits 4.4-7.6) at which the labeled diazoaminobenzene was synthesized.

These results show that the uniformity found in the isotopic compositions of the terminal nitrogen atoms of labeled diazoaminobenzene is undoubtedly due to tautomeric transformations. However, these transformations can not always occur in the course of the reaction which is being investigated, as some of the reactions practically exclude the possibility of tautomeric change (e.g. the thermal decomposition of solid diazoaminobenzene). Clearly, the triazine system is highly mobile, as tautomerism occurs at the instant of formation of diazoaminobenzene from the diazo compound and aniline whatever the pH of the system (within the limits stated above). Consequently the crystalline labeled diazoaminobenzene is actually an equimolecular mixture of the two isotopic isomers (I) and (II), and is not the compound (I) which would have been expected from the method of synthesis.

$$\underset{\text{(I)}}{C_6H_5N^{14}{=}N^{14}N^{15}HC_6H_5} \qquad \underset{\text{(II)}}{C_6H_5N^{14}HN^{14}{=}N^{15}C_6H_5}$$

Hence, the reactions investigated should be expressed by the following equation (1a) - (3a).

$$[{}^1/_2C_6H_5N^{14}{=}N^{14}N^{15}HC_6H_5 + {}^1/_2C_6H_5N^{14}HN^{14}{=}N^{15}C_6H_5] \xrightarrow{CH_3COOH}$$
$$\longrightarrow [{}^1/_2C_6H_5N^{14}{=}N^{14}C_6H_4N^{15}H_2 + {}^1/_2C_6H_5N^{15}{=}N^{14}C_6H_4N^{14}H_2] \longrightarrow$$
$$\xrightarrow{HN^{14}O_2} [{}^1/_2N^{15}N^{14} + {}^1/_2N^{14}N^{14}] \qquad \text{(1a)}$$

$$[{}^1/_2C_6H_5N^{14}{=}N^{14}N^{15}HC_6H_5 + {}^1/_2C_6H_5N^{14}HN^{14}{=}N^{15}C_6H_5] \xrightarrow[\text{pyrolysis}]{HCl \text{ or}}$$
$$\longrightarrow [{}^1/_2N^{14}N^{14} + {}^1/_2N^{14}N^{15}] + [{}^1/_2C_6H_5N^{15}H_2 + {}^1/_2C_6H_5N^{14}H_2] \longrightarrow$$
$$\xrightarrow{HN^{14}O_2} [{}^1/_2N^{15}N^{14} + {}^1/_2N^{14}N^{14}] \qquad \text{(2a)}$$

$$[{}^1/_2C_6H_5N^{14}{=}N^{14}N^{15}HC_6H_5 + {}^1/_2C_6H_5N^{14}HN^{14}{=}N^{15}C_6H_5] \xrightarrow{(C_6H_5)_2C{=}CO}$$
$$\longrightarrow [{}^1/_2C_6H_5N^{14}{=}N^{14}N^{15}\underset{\displaystyle COCH(C_6H_5)_2}{C_6H_5} + {}^1/_2C_6H_5N^{14}N^{14}\underset{\displaystyle COCH(C_6H_5)_2}{{=}N^{15}C_6H_5}] \longrightarrow$$

$$\xrightarrow[\text{or pyrolysis}]{C_2H_5OH,\ CH_3COOH} [{}^1/_2N^{14}N^{14} + {}^1/_2N^{14}N^{15}] + [{}^1/_2C_6H_5N^{15}HCOCH(C_6H_5)_2 +$$

$$+ {}^1/_2C_6H_5N^{14}HCOCH(C_6H_5)_2] \xrightarrow{H_3O^+} [{}^1/_2C_6H_5N^{15}H_2 + {}^1/_2C_6H_5N^{14}H_2] \longrightarrow$$

$$\xrightarrow{HN^{14}O_2} [{}^1/_2N^{15}N^{14} + {}^1/_2N^{14}N^{14}] \qquad (3a)$$

These results are of interest in that it is shown experimentally for the first time: 1) triazines exist in two tautomeric forms (I and II); 2) the triazine system is highly mobile; and 3) the dual reactivity of diazoaminobenzene is not due to the transfer of a reactive center at the time of reaction.

EXPERIMENTAL

I. Preparation of Anthranilic Acid-N^{15} and Aniline-N^{15}

The first of these substances was conveniently prepared by a modification of the method described in the literature [9, 16], which gave a purer product not requiring further purification. To a suspension of 7.35 g of phthalimide-N^{15} in 20 ml of water were added 30 ml of warm (30°) 30% NaOH, and then, with rapid stirring, a cold (0°) solution of sodium hypobromite (2.8 ml Br_2, 9 g NaOH and 25 ml water). The temperature rose to between 60 and 70°, during which the solution should remain colorless. The solution was cooled to 0°, the pH was adjusted to 4 with HCl, and 10-15 ml of glacial acetic acid was added. The yield of anthranilic acid was 80-85%. Aniline-N^{15} was prepared by the known method [9] of pyrolysis of anthranilic acid in a metal bath; yield 95%.

TABLE 1

Results of Mass-Spectrometic Measurements

No	Substance	N^{15} content (atoms %)		Calculation
		Found	Calculated	
1	Initial $N^{15}H_3$*	16.83	–	–
2	Anthranilic acid	8.54	8.60	$\frac{16.83 + 0.38}{2}$
3	Aniline	8.55	8.60	Ditto

To determine the isotopic composition, a known weight of anthranilic acid (or aniline) was diazotized with the theoretical quantity of sodium nitrite and mineral acid. The diazotized solution was placed in one compartment of a two chamber flask, and evacuated (cooling with liquid nitrogen) down to 10^{-4} - 10^{-5} mm. The diazo solution was then mixed with 2.5 moles of cuprous chloride contained in the second compartment, and the nitrogen evolved (yield 99-100%) was analyzed by mass spectrometry.

II. Preparation of Labeled Diazoaminobenzenes

a) Diazoaminobenzene-1(3)-N^{15}. A solution of 0.02 mole of unlabeled aniline in 90 ml of 0.5 N HCl was diazotozed at 0° with 0.02 mole of chemically pure $NaNO_2$. After the disappearance of any excess of nitrous acid, the solution was treated with 300 ml of a 3 molar acetate buffer (pH 6.38)** cooled to 0-5°, held at 0-5° for 15-20 minutes, filtered free from any small amount of precipitated diazoaminobenzene and treated with a solution of 0.02 mole of labeled aniline in 10 ml of methyl alcohol. The mixture was held at 0-5° for 10 minutes, and then the diazoaminobenzene formed was filtered off, carefully washed with water and dried in a vacuum desiccator. Yield 90%; m.p. 97-98°. After one or two recrystallizations from methyl alcohol (1:4) or isooctane (1:10) the melting point rose to 100°.

b) Diazoaminobenzene-2-N^{15}. This was prepared as described above, starting from 0.02 mole of unlabeled aniline and 0.02 mole of $NaN^{15}O_2$.

* The ammonia was oxidized to nitrogen with sodium hypobromite.

** If the reaction is carried out in a more acid or alkaline medium the buffer must be varied accordingly.

TABLE 2

Results of Mass-spectrometric Measurements.

No.	Substance	Reaction	Grouping in which N^{15} was determined	N^{15} content (atoms %) Found	N^{15} content (atoms %) Calculated	Calculation
III, 1	Diazoaminobenzene-1(3)-N^{15}*	Isomerization	Triazine group ****	7.29	7.32	$(21.2 + 2 \cdot 0.38) : 3$
	Aminoazobenzene		Amino group	5.63	5.58	$\left(\frac{21.2 + 0.38}{2} + 0.38\right) : 2$
III, 1	Diazoaminobenzene-2-N^{15}**	Isomerization	Triazine group****	7.21	7.32	$(21.2 + 2 \cdot 0.38) : 3$
	Aminoazobenzene		Amino group	0.38	0.38	
III, 2	Diazoaminobenzene-1(3)-N^{15}*	a) Thermal decomposition	Diazo group	5.61	5.58	$\left(\frac{21.2 + 0.38}{2} + 0.38\right) : 2$
		b) Decomposition in presence of HCl	Diazo group	5.59	5.58	
			Amino group	5.60	5.58	
III, 2	Diazoaminobenzene-1(3)-N^{15}***	a) Thermal decomposition	Diazo group	4.43	4.46	$\frac{16.72 + 0.38}{2} + 0.38 : 2$
		b) Decomposition in presence of HCl	Diazo group	4.41	4.46	
			Amino group	4.40	4.46	
III, 3	Diazoaminobenzene-1(3)-N^{15}***	Acetylation				
		a) Decomposition with alcohol	Diazo group	4.47	4.46	
			Amino group	4.46	4.46	$\left(\frac{16.72 + 0.38}{2} + 0.38\right) : 2$
	Diaphenylacetyldiazoamino-benzene-1(3)-N^{15}	b) Decomposition with acetic acid	Diazo group	4.44	4.46	
		c) Pyrolysis	Diazo group	4.46	4.46	

* Prepared under acid conditions; N^{15} content of original aniline 21.2 atoms %.

** Prepared under acid conditions; N^{15} content of original aniline 21.2 atoms %.

*** Prepared under alkaline conditions; N^{15} content of original aniline 16.72 atom %.

**** To determine N^{15} in the triazine group of diazoaminibenzene, the latter was analyzed by Freund's [18] Kjeldahl method.

III. Transformations of Labeled Diazoaminobenzenes (Table 2)

1. Isomerization to aminoazobenzene. The isomerizations of 2-N^{15}- and 1(3)-N^{15}-diazoaminobenzenes (prepared under acid conditions) were carried out by Rosenhauer's method [10] in the presence of an equimolecular quantity of acetic acid. It was found expedient to do this in vacuo for 5 days at 20°. By this means a purer product was obtained in good yield (87%). The hydrochloride of aminoazobenzene, obtained by Freund's method, was purified by grinding it a few times with acetone or dichloroethane and recrystallizing from 100 volumes of water, slightly acidulated with HCl; for complete recovery it was necessary to raise the concentration of HCl in the filtrate to 2-5% by addition of concentrated HCl. To determine the isotopic composition of the nitrogen in the amino group of aminoazobenzene, the hydrochloride was dissolved by gentle warming in a mixture of 85 % acetic acid and sodium acetate, and diazotized in the usual way, and the diazo compound was decomposed in the presence of 0.6 mole of hydroquinone, using the method described in experiment I (nitrogen yield 99-100%).

2. Decomposition of diazoaminobenzene.

a) Thermal decomposition. About 20 mg of diazominobenzene-1(3)-N^{15} (prepared at pH above or below 7) was heated in an evacuated flask at 10^{-4} - 10^{-5} mm and 150° for 2 hours. The nitrogen evolved (yield 99-100%) was analyzed mass-spectrometrically.

b) Decomposition in the presence of HCl. About 20 mg of diazoaminobenzene-1(3)-N^{15} (prepared at pH above or below 7), was mixed with 1.0 ml of concentrated HCl, evacuated to 10^{-4} - 10^{-5} mm (while the flask was cooled in liquid nitrogen) and heated to 70-80° for 10 minutes. The nitrogen evolved from the diazo group (yield 99-100%) was analyzed mass-spectrometrically, and the residual solution of aniline hydrochloride was diluted with water, after which the isotopic composition of the aniline nitrogen was determined by the method of experiment 1.

3. Acetylation of diazoaminobenzene. The reaction was carried out by Staudinger's [13] method, starting with diazoaminobenzene-1(3)-N^{15} synthesized under alkaline conditions. Carefully dried petroleum and diethyl ethers were used as solvent. The yield of N-diphenylacetyldiazoaminobenzene-1(3)-N^{15} was 88%. Recrystallization from dibutyl ether gave cream colored crystals with an m.p. of 143° (decomp.).

To investigate its isotopic composition, N-diphenylacetyldiazoaminobenzene was: a) heated with alcohol for 10 minutes at 70-80°; b) heated with acetic acid for 10 minutes. In each case the reaction was thermally at 143° for 10 minutes. In each case the reaction was performed in a flask evacuated to 10^{-4} - 10^{-5} mm; and the yield of nitrogen was 99-100%.

The diphenylacetanilide, obtained by the decomposition of N-diphenylacetyldiazoaminobenzene in the presence of alcohol, was recrystallized from C_2H_5OH and hydrolyzed to aniline with 20 % HCl (1 ml to 60 mg of material). This required heating for 9 hours in a sealed tube at 160°. The isotopic composition of the aniline nitrogen was determined as described under experiment I.

SUMMARY

A new method, using labeled atoms, has been proposed for investigating dual reactivity and tautomerism. The method has been applied to elucidate the character of the triazine (diazoamino) group in diazoaminobenzene.

It has been shown, for the first time, that triazines exist in two tautomeric forms, that the triazine system is highly mobile and that the dual reactivity of diazoaminobenzene is not caused by the transfer of a reactive center at the time of reaction.

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RESEARCH IN THE FIELD OF SUBSTITUTED 1,5-DIPHENYLTHIOCARBAZONES

V. SYNTHESIS OF ALKYL- AND ARYL-SUBSTITUTED 1,5-DIPHENYLTHIOCARBAZONES

P. S. Pelkis, L. S. Pupko and R. G. Dubenko

Alkyl-substituted dithizones were first obtained by Freund. He synthesized o- and p-tolylthiocarbazones by the hydrazine method of E. Fischer [1]. Suprunovich obtained di-(β-naphtyl)-thiocarbazones by the hydrazine method and investigated the sensitivity of o-tolyl and β-naphthyl-thiocarbazones for the detection of metallic ions [2]. Hubbard and Scott synthesized o- and p-tolyl- and α- and β-naphthylcarbazones by the formazyl method, and determined their sensitivity for the detection of mercury ions [3]. P. S. Pelkis and L. S. Pupko synthesized o-, m- and p-tolylthiocarbazones by the hydrazine and formazyl methods, and investigated their metallic complexes spectrophotometrically [4]. Tarbell and his co-workers synthesized o-, m- and p-biphenylthiocarbazones [5], but only investigated di-(p-biphenyl)-thiocarbazone spectrometrically [6]. Oesper and Klingenberg [7] synthesized di-(2,4-dimethylphenyl)-thiocarbazone by the formazyl method, and tested it qualitatively with the cations of Hg, Cd, Zn, Bi and Ag. Their spectrometric results were similar to ours. However, both their formazyl derivative and their thiocarbazone had melting points considerably below those of definitely pure samples. Their nitroformazyl derivative melted at 146-148°, and the thiocarbazone at 152-154°, compared with our figures of 157-158° and 163-164°, respectively.

The thiocarbazones shown below were synthesized from the corresponding amines by the formazyl method [3, 8], via their nitroformazyl derivatives, according to the following scheme

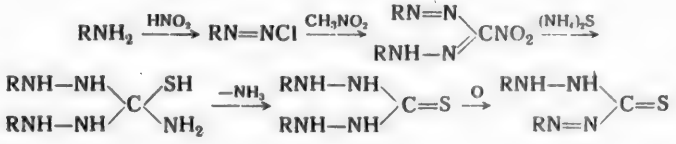


Table 1 shows data obtained with pure samples of the nitroformazyl derivatives. These were all prepared by the method described below. The reaction between the diazoniumsalt and nitromethane was carried out in a mixture of glacial acetic acid and sodium acetate (mol. ratio 1:1.5), which gave better yields of the nitroformazyl derivative (60-90%) than with alkaline nitromethane as solvent [3]. The nitroformazyl derivatives, except for 1,5-di-(2-methyl-5-isopropylphenyl)-3-nitroformazyl (Table 1, No. 8) were crystalline compounds. They were purified by reprecipitation from alkaline alcoholic solution with dilute hydrochloric acid. Traces of solvent were removed in vacuo.

The nitroformazyl crystals were in the shape of needles or platelets, often with a metallic sheen, orange-red or cherry-red in color, and frequently melted with decomposition. They dissolved in most organic solvents, but were sparingly soluble in ethanol or methanol.

Thiocarbazones are crystalline substances, dark red, brown or black in color, often with a metallic sheen. They dissolve in benzene, carbon tetrachloride, chloroform, dichloroethane, acetone and other organic solvents to give green solutions. An exception is the thiocarbazone obtained from dehydrothiotoluidine¶(Table 3, substance 13), which is sparingly soluble in acetone and insolubel in ether or benzene.

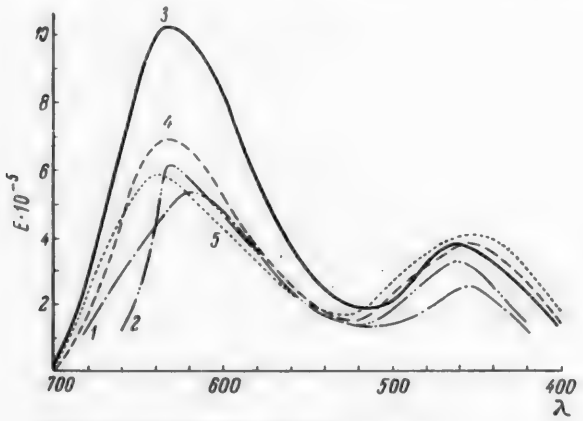
¶ Probable Russian misprint — Publisher's note.

TABLE 1

Nitroformazyls of the General Formula $RN{=}N\diagdown\!\!\diagup CNO_2$ (RNH—N)

No.	R	Yield %	Melting point	Empirical formula	Nitrogen content %	
					Found	Calculated
1	2,4-Xylyl	97	157—158° (decm)	$C_{17}H_{19}O_2N_5$	21.78, 21.66	21.54
2	2,5-Xylyl	67	154—155 (decm)	$C_{17}H_{19}O_2N_5$	21.77, 21.51	21.54
3	3,4-Xylyl	97	170—171	$C_{17}H_{19}O_2N_5$	21.42, 21.74	21.54
4	o-Ethylphenyl.	83	89—90	$C_{17}H_{19}O_2N_5$	21.71, 21.69	21.54
5	p-Ethylphenyl.	79	103—104	$C_{17}H_{19}O_2N_5$	21.43, 21.38	21.54
6	m-Ethylphenyl	72	Oil	$C_{17}H_{19}O_2N_5$	21.36, 21.21	21.54
7	p-Isopropylphenyl	84	116—117 (decm)	$C_{19}H_{23}O_2N_5$	20.02, 19.98	19.83
8	2-Methyl-5-iospropylphenyl	65	Oil	$C_{21}H_{27}O_2N_5$	18.11, 18.23	18.37
9	p-n-Butylphenyl	76	114—115	$C_{21}H_{27}O_2N_5$	18.52, 18.40	18.37
10	p-Tert-butylphenyl	50	127—128 (decm)	$C_{21}H_{27}O_2N_5$	18.20, 17.98	18.37
11	β-Tetralyl.	61	179—180 (decm)	$C_{21}H_{23}O_2N_5$	18.24, 18.31	18.57
12	p-(5-Methyl-benzothiazolyl-2)-phenyl.	73	212—214 (decm)	$C_{29}H_{21}O_2N_7S_2$	17.13, 17.09	17.41
13	2-Methyl-benzothiazolyl-6	88	165—167	$C_{17}H_{13}O_2N_7S_2$	23.39, 23.48	23.84

Table 3 shows the absorption maxima of the thiocarbazones, their molar extinction coefficients at the long and short wave maxima and α, the ratio of the latter.



Ultraviolet Absorption Spectra.

1) 1,5-diphenylthiocarbazone; 2) 1,5-di-(4-isopropylphenyl)-thiocarbazone; 3) 1,5-di-(tetrahydro-β-naphthyl)-thiocarbazone; 4) 1,5-di-(4-tert-butylphenyl)-thiocarbazone; 5) 1,5-di-(2-methyl-5-isopropylphenyl)-thiocarbazone.

TABLE 2

Alkyl and Aryl Thiocarbazones of the General Formula $RNH-NH\diagdown C=S$ / $RN=N\diagup$

No.	R	Yield %	Melting point	Empirical formula	Nitrogen content	
					Found	Calculated
1	2,4-Xylyl	29	163—164°	$C_{17}H_{20}N_4S$	17.65, 17.72	17.95
2	2,5-Xylyl	23	148—149	$C_{17}H_{20}N_4S$	17.74, 17.82	17.95
3	2,3-Xylyl	27	139—140	$C_{17}H_{20}N_4S$	17.70, 17.81	17.95
4	3,4-Xylyl	24	141	$C_{17}H_{20}N_4S$	18.00, 18.10	17.95
5	o-Ethylphenyl	28	122—123	$C_{17}H_{20}N_4S$	18.20, 18.10	17.95
6	m-Ethylphenyl	30	Oil	$C_{17}H_{20}N_4S$	17.58, 17.62	17.95
7	p-Ethylphenyl	28	103—104	$C_{17}H_{20}N_4S$	18.15, 18.20	17.95
8	p-Isopropylphenyl	70	110—111	$C_{19}H_{24}N_4S$	16.65, 16.59	16.47
9	p-n-Butylphenyl	29	120—121	$C_{21}H_{28}N_4S$	14.92, 15.05	15.22
10	p-Tert-butylphenyl	49	137	$C_{21}H_{28}N_4S$	15.29, 15.34	15.22
11	2-Methyl-5-isopropylphenyl	59	127	$C_{21}H_{28}N_4S$	15.19, 15.25	15.22
12	β-Tetralyl	22	135	$C_{21}H_{24}N_4S$	15.22, 15.12	15.40
13	p-(5-Methylbenzothiazolyl--2)-phenyl	28	236	$C_{29}H_{22}N_6S_3$	14.96, 15.01	15.27

TABLE 3

Arylthiocarbazones of the General Formula $RNH-NH\diagdown C=S$ / $RN=N\diagup$

No.	R	λ_{max_1} (in mμ)	λ_{max_2} (in mμ)	$E_{max_1} \cdot 10^4$	$E_{max_2} \cdot 10^4$	$\alpha = \frac{E_2}{E_1}$
1	Phenyl**	450	620	4.6	7.9	1.72
2	o-Tolyl**	470	632	4.8	12.3	2.56
3	m-Tolyl**	465	635	5.5	11.4	2.07
4	p-Tolyl**	465	630	6.4	14.5	2.27
5	o-Ethylphenyl	455	635	4.08	8.8	2.15
6	p-Ethylphenyl	445	635	6.8	10.2	1.5
7	m-Ethylphenyl	445	630	6.3	7.04	1.12
8	p-Isopropylphenyl	455	630	5.17	11.7	2.26
9	p-n-Butylphenyl	455	635	6.5	13.74	2.11
10	p-Tert-butylphenyl	455	630	7.8	14.2	1.82
11	2,4-Xylyl**	470	640	5.3	15.05	2.84
12	2,5-Xylyl	460	635	5.05	11.4	2.26
13	2,3-Xylyl	465	640	4.5	12.6	2.8
14	3,4-Xylyl	460	635	4.95	13.65	2.76
15	2-Methyl-5-isopropylphenyl	450	640	8.4	11.9	1.42
16	p-Biphenyl**	490	655	5.2	10	1.92
17	β-Napthyl**	—	662	—	10.3	—
18	α-Napthyl**	—	683	—	11.5	—
19	β-Tetralyl**	465	635	7.4	20.5	2.77
20	p-(5-Methyl-benzothiazolyl--2)-phenyl	480	680	6.5	18.1	2.78

* Substance 1-16 and 19 were dissolved in benzene, 18, in carbon tetrachloride and 20, in chloroform.

** Thiocarbazones described in the literature.

The absorption spectra were measured with an electric spectrophotometer type SF-4. The solutions used were $6.6 \cdot 10^{-5}$ M. For all the thiocarbazones in Table 3 the extinction coefficient was greater at the long wavelength than at the short wavelength maximum. As we have shown previously [9], the value of α is determined by the condition of the thione-thiol equilibrium in the solvent used.

With the naphthylthiocarbazones the short wave maxima are missing, so that, in solution, these compounds exist only in the thione form. The figure shows the absorption curves of some alkyl and aryl thiocarbazones.

EXPERIMENTAL

The substances in Tables 1 and 2 were synthesized by the formazyl method. The synthesis of a single thiocarbazone is described below. All the others were prepared similarly.

1,5-Di-(4-isopropylphenyl)-thiocarbazone was obtained from 1,5-di-(4-isoproylphenyl)-3-nitroformazyl, which was synthesized as follows: 5 g of p-cymidine were added with cooling and stirring to a mixture of 15 ml of concentrated hydrochloric acid and 31 ml of water. After cooling to 0° the amine was diazotized with 2.7 g of sodium nitrite in 14 ml of water. At the diazotizing concentration everything dissolved. With vigorous stirring, the solution of the diazonium salt was poured into a mixture of 163 g of sodium acetate and 81 ml of glacial acetic acid. Nitromethane (6.3 g) was added in the course of 10-15 minutes, and the whole was then stirred for 5 hours. The red precipitate of the formazyl derivative was filtered off, washed with water till neutral and dried at 60°. Yield 5.5 g (84 %). Reprecipitation from dioxan with methanol gave shining red needles.

The nitroformazyl derivative (0.5 g) was taken up in 100 ml of alcohol, and gaseous ammonia and hydrogen sulfide were passed through until the color of the solution changed from red to yellow. The solution was poured o on to ice, and the di-(4-isoprpylphenyl)-thiocarbohydrazide formed was filtered off and carefully washed with water. The product was agitated in the cold with a 5% alcoholic solution of caustic potash for 10 minutes. The solution was diluted with water, and the thiocarbazone was precipitated by stirring in 2% hydrochloric acid until there was an acid reaction to congo paper. The thiocarbazone separated in the form of dark red needles with a metallic sheen. Melting point 110-111° (decomposes). Yield 0.2 g (70%).

SUMMARY

Thirteen nitroformazyl derivatives and thirteen alkyl and aryl substituted 1,5-diphenylthiocarbazones have been synthesized.

The absorption spectra of the arylthiocarbazones have been investigated.

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INVESTIGATIONS IN THE FIELD OF SUBSTITUTED 1,5-DIPHENYLTHIOCARBAZONES

V. THE SYNTHESIS OF ALKOXY- AND ARYLOXY-SUBSTITUTED 1,5-DIPHENYLTHIOCARBAZONES

P. S. Pelkis, R. G. Dubenko and L. S. Pupko

In the previous paper [1] the synthesis of alkyl- and aryl-substituted 1,5-diphenylthiocarbazone was described and the results of the spectrophotometric investigation of synthesized compounds were given.

It was of interest to synthesize and study the properties of derivatives of 1,5-diphenylthiocarbazone with alkoxy- and aryloxy groups as substituents. Tarbell and his co-workers described the synthesis of o-methoxy, o-ethoxy, o-and p-phenoxy, o-methylmercapto- and o-phenylmercapto-substituted 1,5-diphenylthiocarbazone [2]. The absorption spectra of the synthesized arylthiocarbazones were not given in the article.

We synthesized alkoxy- and alkylmercapto derivatives of 1,5-diphenyl-thiocarbazone by the formazyl method [3]. The nitroformazyl derivative are given in Table 1. They are crystalline substances, usually small colored needles or platelets, crystallizing from methyl alcohol, dioxan or a mixture of these solvents, soluble in hydrocarbons, ethers and ketones and difficultly soluble in methyl alcohol and carbon tetrachloride.

TABLE 1

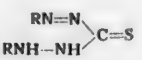
Nitroformazyl Derivative with the General Formula

Exp No.	R	Yield (as %)	Melting point	Empirical formula	Nitrogen analysis (as %)	
					Found	Calculated
1	m-Anizyl	72	135°	$C_{15}H_{15}O_4N_5$	21.07, 21.14	21.28
2	p-Anizyl	87	155	$C_{15}H_{15}O_4N_5$	21.05, 21.23	21.28
3	m-Phenetyl	50	127	$C_{17}H_{19}O_4N_5$	19.62, 19.80	19.60
4	p-Phenetyl	96	158	$C_{17}H_{19}O_4N_5$	19.30, 19.40	19.60
5	o-Isopropoxyphenyl	83	141	$C_{19}H_{23}O_4N_5$	18.36, 18.48	18.18
6	o-N-Butoxyphenyl	88	82—83	$C_{21}H_{27}O_4N_5$	16.68, 16.75	16.95
7	o-Isoamyloxyphenyl	89	98—99	$C_{23}H_{31}O_4N_5$	15.80, 15.75	15.87
8	p-Methylmercaptophenyl	85	158	$C_{15}H_{15}O_2N_5S_2$	19.08, 19.14	19.39
9	p-Trifluoromethylmercaptophenyl	55	163	$C_{15}H_9O_2N_5S_2F_6$	14.90, 15.07	14.92

The corresponding arylthiocarbazones are given in Table 2. They are colored crystalline compounds; they dissolve in organic solvents, producing a green or blue-green color and are difficultly soluble in methyl alcohol. The compounds were purified by reprecipitating from alcoholic alkaline solutions with dilute sulfuric acid, then reprecipitated from a chloroform solution by methyl alcohol and dried at 50° under vacuum.

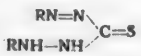
The arylthiocarbazones were investigated spectrophotometrically. The measurements were made in benzene at a solution concentration of $6.6 \cdot 10^{-5}$ moles using an SF-4 spectrophotometer.

TABLE 2

Arylthiocarbazones with the General Formula 

Exp No.	R	Yield (as %)	Melting point	Empirical formula	Nitrogen analysis (as %)	
					Found	Calculated
1	m-Anizyl	51	142—143°	$C_{15}H_{16}O_2N_4S$	17.63, 17.51	17.72
2	p-Anizyl	63	136	$C_{15}H_{16}O_2N_4S$	17.42, 17.58	17.72
3	m-Phenetyl	23	140	$C_{17}H_{20}O_2N_4S$	16.03, 16.10	16.28
4	p-Phenetyl	32	129	$C_{17}H_{20}O_2N_4S$	16.53, 16.45	16.28
5	o-Isopropoxyphenyl	74	135	$C_{19}H_{24}O_2N_4S$	15.18, 15.10	15.05
6	o-N-Butoxyphenyl	78	136	$C_{21}H_{28}O_2N_4S$	14.17, 14.20	14.00
7	o-Isoamyloxyphenyl	70	141—142	$C_{23}H_{32}O_2N_4S$	13.35, 13.25	13.08
8	p-Methylmercaptophenyl	63	132	$C_{15}H_{16}N_4S_3$	16.39, 16.25	16.10
9	p-Trifluoromethylmercaptophenyl	44	136	$C_{15}H_{10}N_4S_3F_6$	12.54, 12.35	12.28

TABLE 3

Arylthiocarbazones with the General Formula 

Exp No.	R	λ_{max_1} (a mμ)	λ_{max_2} (a mμ)	$E_1 \cdot 10^4$	$E_2 \cdot 10^4$	$\alpha = \frac{E_2 \cdot 10^4}{E_1 \cdot 10^4}$
1	Phenyl*	450	620	4.60	7.90	1.72
2	o-Anizyl*	486	659	6.50	15.30	2.35
3	m-Anizyl	465	634	5.56	11.03	1.98
4	p-Anizyl	476	646	6.11	18.10	2.96
5	o-Phenetyl*	480	655	6.40	16.30	2.54
6	m-Phenetyl	470	635	5.94	12.76	2.15
7	p-Phenetyl	465	646	5.50	18.54	3.37
8	o-Isopropoxyphenyl	460	650	3.46	11.80	3.41
9	o-N-Butoxyphenyl	496	655	3.80	12.50	3.30
10	o-Isoamyloxyphenyl	500	655	3.47	11.97	3.45
11	o-Phenoxyphenyl*	480	650	3.60	8.40	2.33
12	o-Methylmercaptophenyl	475	640	6.96	13.15	1.89
13	p-Methylmercaptophenyl	530	675	9.14	16.44	1.80
14	p-Trifluoromethylmercaptophenyl	450	640	10.37	11.30	1.09

Table 3 gives data on the measurement of the absorption spectra of thiocarbazones, molar extinctions in the region of maxima and the value of α, the ratio of the extinctions.

The introduction of alkoxy- and aryloxy groups as substituents in the phenyl groups of diphenylthiocarbazone displaces the long-wave maximum towards the long waves by 15-39 mμ and the short-wave maximum by 10-15 mμ. Minimum displacement is found with introduction of an alkoxy group in the meta position, maximum displacement with introduction in the para position. The powerful bathochromic influence of alkoxy- and aryloxy groups in the ortho and para positions of the phenyl groups is evidently connected with the elongation effect of a conjugated chain.

Absorption curves with greater extinctions in the region of the long-wave maximum than in the short-wave

* The compounds noted with an asterisk are described in literature.

region are characteristic for both this series of compounds and those previously described by us. Fig. 1 shows the absorption curves of several compounds of this group of thiocarbazones.

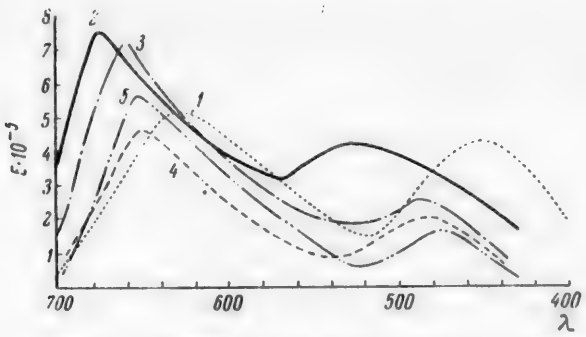


Fig. 1. Absorption spectra in the ultraviolet region of substitued thiocarbazoles

1) 1,5-di-(4-phenetyl)-thiocarbazone. 2) 1,5-di-(4--methylmercaptophenyl)-thiocarbazone. 3) 1,5-di--(2-anizyl-)-thiocarbazone. 4) 1,5-di-(2-phenoxyphenyl)--thiocarbazone. 5) 1,5-di-(4-anizyl)-thiocarbazone.

With the introduction of a trifluoromethylmercapto group as a substituent in the para position to the thiocarbazone group a slight displacement of the absorption maxima occurs; the intensity of the long-wave maximum decreases, however, the intensity of the short-wave maximum increases and the value of α is 1.1, i.e. the thionic--thiolic equilibrium is shifted towards the thiolic form.

EXPERIMENTAL

The compounds whose data are given in Tables 1 and 2 were synthesized by the formazyl method, with slight modifications of the latter; the typical conditions of synthesis for one of the thiocarbazones are, therefore, given below.

1,5-Di-(4-methylmercaptophenyl)-thiocarbazone. 4-Methylmercaptoaniline was obtained from 4-methylmercapto-1-nitrobenzene by the reduction of the latter with zinc dust in hydrochloric acid [4]. It is an oil with b.p. 140° (15 mm).

2 g of 4-methylmercaptoaniline was dissolved in 20 cc of 15 % hydrochloric acid and diazotized by adding 0.6 g of sodium nitrite in 4 cc of water and mixing with a mechanical stirrer (temperature 0°). The clear diazo solution was added to a mixture of 80 g of sodium acetate and 40 g of glacial acetic with intensive stirring. The solution was colored green. After 10 minutes 1.5 g of nitromethane was added and the mixture stirred for a further 4 hours. The color changed to dark-red. The precipitate was filtered, washed with water, then with a small quantity of alcohol and ether and dried under vacuum. After recrystallization from dioxan the crystals had a dark-cherry color. The m.p. was 157-158° (decomp.). The yield was 2.2 g (85%). The product was soluble in the majority of organic solvents, giving a bright-violet color; it was difficultly soluble in alcohol.

0.5 g of the formazyl derivative was suspended in 100 cc of alcohol and the suspension was saturated with gaseous ammonia and hydrogen sulfide until it dissolved. The solution which had a cherry-violet color was poured on to ice and the violet crystalline precipitate of thiocarbazide was filtered off and washed with water. The thiocarbazide was treated with 2% alcoholic alkali for 15 minutes in the cold. Dark-blue thiocarbazone was precipitated by 1% hydrochloric acid from the dark-red alcoholic alkaline solution. After reprecipitating twice with dilute hydrochloric acid from an alcoholic alkaline solution the thiocarbazone was filtered off and washed with water and a small quantity of alcohol and ether. It was in the form of dark-blue crystals with m.p. 131-132°. The yield was 0.18 g (37%). It was soluble in organic solvents, giving a dark-green color.

SUMMARY

1. 9 alkoxy-substituted 1,5-diphenyl-3-nitroformazanes and 9 alkoxy-substituted 1,5-diphenylthiocarbazones were synthesized.

2. The synthesized arylthiocarbazones were investigated spectrophotometrically. It was found that by the introduction of alkoxy or aryloxy groups as substituents in the phenyl groups of dithizone the absorption maxima of thiocarbazones are displaced into the long-wave region.

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THE SYNTHESIS OF 2,5 AND 2,5'-DIPHENYL-HEXAHYDRO-(3,4 : 3',4')-FUROFURANES

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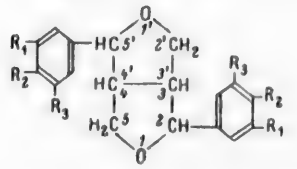
The heterocyclic condensed system of hexahydro-(3,4 : 3',4')-furofuran forms the basis of a specific group of natural substances, the so-called phenol resinols or lignanes. The following compounds are included in this group: pinoresinol (I; $R_1 = CH_3O$, $R_2 =$ OH, $R_3 =$ H), eudesmin (I; $R_1 = R_2 = CH_3O$, $R_3 =$ H), sesamin (I; $R_1 =$ $= R_2 = H_2C\langle^{O-}_{O-}$, $R_3 =$ H) and syringaresinol (I; $R_1 = R_3 = CH_3O$, $R_2 =$ OH).

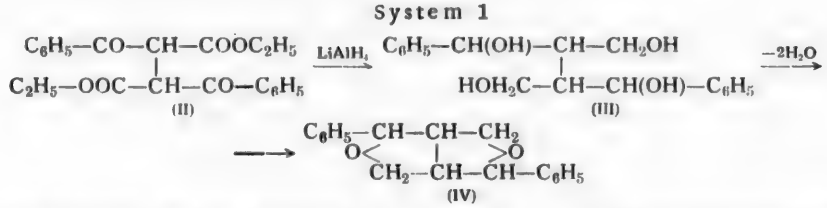


(I)

This series of substances is interesting from the aspect of their biological action; in particular, one of these compounds, sesamin, is biologically active with respect to pathogenic bacteria, particularly Mycobacterium tuberculosis, whose development is inhibited by sesamin at a dilution of 1 : 10 million [1,2]. Sesamin also considerably intensifies the insecticidal action of pyrethrin [3,4].

Synthetic methods for preparing substances of this group were only very recently developed. DL-pinoresinol [5] was recently synthesized from ferulic acid, and DL-syringaresinol [6] from sinapic acid. Only resinols with free phenolic hydroxyls can be obtained, however, by this method. It was of interest to develop a general method for obtaining compounds of the series 2,5- and 2,5'-diaryl-hexahydro-(3,4 : 3',4')-furofuran With this aim the parent substance of this group, 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran (I; $R_1 = R_2 = R_3 =$ H), was synthesized. The method we selected is represented by the system

System 1

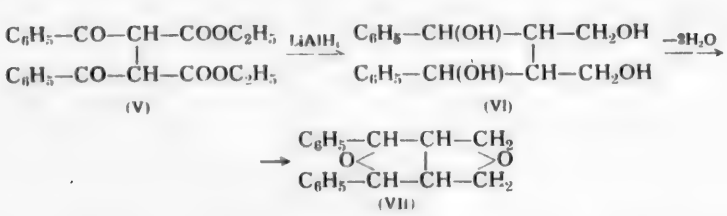


The initial substance used for the synthesis was one of the isomers of dibenzoylsuccinic ester (II) which was converted by reduction with lithium aluminiumhydride into the corresponding 2,3-di-(α-hydroxybenzyl)-1,4-butanediol (III). Dehydration of the latter by heating with potassium bisulfate gave 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran (IV). The configuration of the initial dibenzoylsuccinic ester was of particular importance for carrying out this synthesis. The bis-ketonic form of dibenzoylsuccinic ester was obtained as two stereoisomeric forms, one of which was the meso form and the other the racemate. Without experimental proof, Knorr [7] assumed the structure of the meso form for the low-melting isomer which he called the γ-ester and the racemate structure for the high-melting isomer, the so-called β-ester. By reducing each of the isomers with lithium aluminiumhydride their corresponding diastereoisomeric tetraols could be formed: two meso forms and one racemate from the meso form and three racemic forms from the racemic ester. Starting from the dibenzoylsuccinic esters we obtained two individual tetraols: one of these, obtained by reduction of the β-dibenzoylsuccinic ester, had an m.p. of 128-130° (we named this provisionally β-tetraol) (VI), the other, obtained by the reduction of γ-dibenzoylsuccinic ester, had an m.p. of 74-78° (we called this γ-tetraol) (III). Both tetraols were character-

ized in the form of their tetracetates. The oily substances remaining after the separation of the crystalline tetraols also contained hydroxyl groups and possibly also included other isomers.

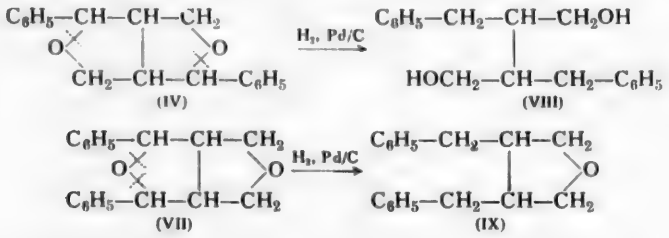
The individual tetraols were dehydrated: a) by heating with 50 % sulfuric acid, b) by heating with potassium bisulfate, c) by distillation under vacuum, d) by heating under vacuum in the presence of potassium bisulfate. It was found that heating β-tetraol at 140° for 10 hours with 50%sulfuric acid, or heating it at 180° for 30 minutes with potassium bisulfate results in considerable tarring. When heating under vacuum β-tetroal distilled without serious decomposition at 300-320° (0.03 mm). The γ-tetraol (III) was dehydrated by heating under vacuum at 150-200° (13 mm) in the presence of potassium bisulfate; a crystalline substance with an m.p. of 72.5-74° was formed, corresponding by analysis to the composition $C_{18}H_{18}O_2$, i.e. tothe product obtained by splitting off two molecules of water from tetraol. The cyclization of β-tetraol (VI) was carried out under the same conditions at 110-170° (9 mm), a compound of the same composition with m.p. 88.5-90° being obtained. Neither of these substances contained hydroxyl groups or double bonds. It could be assumed that one of these compounds was the desired 2,5'-diphenyl-substituted hexahydro-(3,4 : 3',4')-furofuran and the second its isomeric 2,5-diphenyl compound whose formation may be represented according to system 2.

System 2

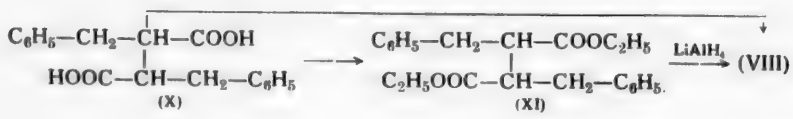


In order to prove that structure of the substances obtained we subjected both these compounds to catalytic hydrogenation in the presence of palladium on charcoal. On the basis of known data on the hydrogenation of benzoyl esters [8] it was to be expected that 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran would be completely split up to give 2,3-dibenzyl-1,4-butanediol (VIII), but that as a result of partial splitting 2,5-diphenyl-hexahydro-(3,4 : 3',4')-furofuran would give 3,4-dibenzyl-tetrahydrofuran (IX) according to system 3.

System 3



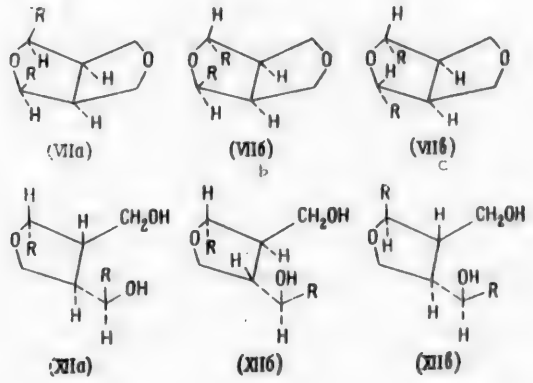
As a result of the hydrogenation of the isomer with m.p. 72.5-74° a substance with m.p. 87-88° was obtained whose analysis and properties corresponded to 2,3-dibenzyl-1,4-butanediol (VIII). The structure of this substance was confirmed by comparing it with a sample obtained by the reduction with lithium aluminiumhydride of DL-dibenzyl-succinic acid (X) and its diethyl ester (XI).



It was, therefore, proven that the diphenyl-hexahydro-(3,4 : 3',4')-furofuran with m.p. 72.5-74° is 2,5'-disubstituted hexahydro-(3,4 : 3',4')-furofuran (IV). Hydrogenation of the isomeric compound with m.p. 88.5-90° led to the formation of a substance with m.p. 65.5-67° which did not contain hydroxyl groups and whose analysis corresponded to 3,4-dibenzyl-tetrahydrofurane. From this it follows that the isomer with m.p. 88.5-90° is 2,5--diphenyl-hexahydro-(3,4 : 3',4')-furofurane (VII).

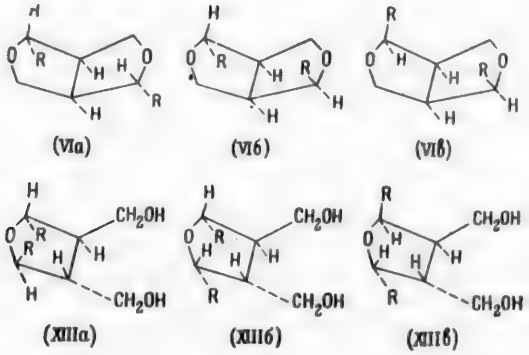
The proof of the structure of 2,5- and 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofurans can serve as a basis for explaining the structure of the initial dibenzoylsuccinic esters which has not been hitherto established. Taking into consideration the possibilities of ring closure to form hexahydro-furofuran rings in the case of teraols, obtained by the reduction of meso-dibenzoylsuccinic ester and its racemate, the following conclusion may be drawn. On reduction the meso-form of dibenzoylsuccinic ester gives tetraols which cannot easily form 2,5'-diphenyl--hexahydro-(3,4 : 3',4')-furofuran without stresses arising since when closure of one ring takes place by the primary and secondary hydroxyls the primary and secondary hydroxyls of the second pair are in the trans-position to each other (system A; XIIa, b, c).

System A



On the other hand, dehydration can easily take place in these tetraols by the interaction of two primary and two secondary hydroxyls, i.e. the formation of 2,5-diphenyl-hexahydro-(3,4 : 3',4')-furofuran (system A; VIIa, b, c). For tetraols, obtained by the reduction of the racemic dibenzoylsuccinic ester, a correspondingly easy dehydration with the formation of 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran (system B; VIa, b, c) and a corresponding difficulty in forming 2,5-substitued derivatives from diols (system B; XIIIa, b, c) may be assumed.

System B



In consequence, the proof of the structure of the diphenyl-hexahydro-(3,4 : 3',4')-furofurans obtained allows the conclusion to be drawn that, in contrast to Knorr's assumption, the dibenzoylsuccinic ester with m.p. 128-130°

(the β-ester) is evidently the meso-form and the γ-ester (m.p. 74-78°) is the racemate.

The method we developed for synthesizing 2,5- and 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofurans may also be used for obtaining derivatives substituted in the benzene rings, i.e. natural resinols. We used this method to obtain DL-sesamin, commencing the synthesis with the oily isomer of dipiperonyl-succinic ester which is, therefore, also the racemate. Just as our investigations were completed, however, the work of Beroza [9] and Freudenberg [10], who also obtained DL-sesamin by a similar method, was published. The constants of the compounds which we synthesized [1,4-di-(3',4'-methylenedihydroxyphenyl)-2,3-dihydroxymethyl-1,4-butanediol m.p. 158° and DL-sesamin, m.p. 126°] coincide with those published [10].

In order to obtain substituted diphenyl-hexahydro-(3,4 : 3',4')-furofurans we attempted an explanation of the possibility of the direct introduction of substituents in the aromatic rings. The nitration of both isomers was investigated. The dinitroderivative was obtained from 2,5-diphenyl-hexahydro-(3,4 : 3',4')-furofurane by nitration with nitric acid (d 1.5) in glacial acetic acid. It had not been hitherto possible to find conditions for nitrating 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran . Under mild conditions the initial substance was recovered unchanged but with more intensive nitration destructive oxidation took place; a substance which had the properties of an aldehyde and contained hydroxyl groups was obtained. Work in this direction is continuing.

EXPERIMENTAL

1. Meso-2,3-di-(α-hydroxybenzyl)-1,4-butanediol (III). To a suspension of 3.25 g of lithium aluminium-hydride in 320 cc of absolute ether, cooled to 0°, 8.7 g of β-dibenzoylsuccinic ester [7] (m.p. 128-129°) in 460 cc of absolute ether was gradually added with stirring at such a rate that the temperature of the reaction mass did not exceed 4°. The mixture was stirred for 2 hours at 20° and for 1 hours at the boiling point of ether. The reaction mass, cooled to 0°, was carefully decomposed with 40 cc of water, then with 20% dilute sulfuric acid (until a weak reaction to congo paper was obtained). The ethereal solution was decanted from the precipitate, dried with sodium sulfate and evaporated under vacuum. The light-yellow viscous oil remaining was dried in a vacuum desiccator. After shaking with anhydrous ether 1.82 g of crystalline substance with m.p. 122-135° was obtained. A further 1.65 g of the same substance with m.p. 130-136° was obtained by evaporation of the mother liquor. The total yield of meso-2,3-di-(α-hydroxybenzoyl)-1,4-butanediol was 50.4%. It was in the form of colorless prisms with m.p. 137-138.5° (from dichloroethane), soluble in acetone, ethyl acetate, dioxan , ether, alcohol and acetic acid; difficultly soluble in dichloroethane, chloroform and water; insoluble in carbon tetrachloride.

Found %: C 71.32; H 7.58; OH 22.25. $C_{18}H_{22}O_4$. Calculated %: C 71.52; H 7.28; OH 22.50.

Tetracetate. A mixture of 1 g of meso-2,3-di(α-hydroxybenzyl)-1,4-butanediol, 4.05 g of acetic anhydride and 0.4 g of freshly-melted potassium acetate was heated with moderate boiling for 1 hour 30 minutes. After cooling to 40-50° the reaction mass was diluted with 40.5 cc of water and kept for 2 hours at room temperature; the oil which separated out was extracted with ether, the extracts were washed with bicarbonate solution, dried over sodium sulfate and evaporated under vacuum. The oily substance which remained crystallized out on the addition of a small quantity of anhydrous ether. After filtering and washing with absolute ether 0.57 g of a substance with m.p. 139-143° was obtained; a further 0.09 g of this substance was obtained by evaporation of the mother liquor. The total yield of the meso-2,3-di-(α-hydroxybenzyl)-1,4-butanediol tetracetate was 41.5%. It was in the form of colorless prisms (from ethyl alcohol) with m.p. 112-113°, soluble in dioxan ether, acetone, ethyl acetate, benzene, chloroform and dichloroethane; difficultly soluble in alcohol and acetic acid; insoluble in water.

Found %: C 65.98; H 6.47; $COCH_3$ 31.8. $C_{26}H_{30}O_8$. Calculated %: C 66.38; H 6.38; $COCH_3$ 36.6.

Tetrabenzoate. 8.5 cc of anhydrous pyridine and 3.7 g of freshly-distilled benzoyl chloride were added to 0.8 g of meso-2,3-di-(α-hydroxybenzyl)-1,4-butanediol in 10 cc of anhydrous chloroform and the mixture allowed to stand overnight. Dilute sulfuric acid was then added until an acid reaction was obtained; the chloroform layer was separated and the aqueous layer extracted with chloroform. The extracts were washed with a bicarbonate solution, dried over sodium sulfate and evaporated under vacuum. The benzoic acid formed was filtered off and the mother liquor diluted with anhydrous alcohol. After the precipitate of meso-2,3-di-(α-hydroxybenzyl)-1,4-butanediol tetrabenzoate had been filtered and washed it was dried in a vacuum desiccator. The yield was 0.28 g, the m.p. 254-257.5° (softening at 240°). A further 0.32 g of this substance was obtained by evaporation of the mother liquor. The total yield of the tetrabenzoate was 32%. It was in the form of colorless crystals, m.p. 258-259°

from dioxan), soluble in dichloroethane, chloroform and benzene; difficultly soluble in diozan insoluble in ether, acetone, ethyl acetate, acetic acid and water.

Found %: C 76.44;; H 5.68. $C_{46}H_{38}O_8$. Calculated %: C 76.88; H 5.29

2. DL-2,3-Di-(α-hydroxybenzyl)-1,4-butanediol. 32.47 g of γ-dibenzoylsuccinic ester [7] (m.p. 74-78°) in 570 cc of absolute ether was reduced with 12.1 g of lithium aluminiumhydride in 300 cc of absolute ester under the conditions described for the reduction of β-dibenzoylsuccinic ester. 8 g (31%) of DL-2,3-di-(α-hydroxybenzyl)-1,4-butanediol with m.p. 130-144° was obtained; after recrystallizing twice (from dichloroethane) the m.p. was 147.5-148°. It was in the form of colorless prisms, soluble in ether, alcohol, acetone and ethyl acetate, and difficultly soluble in dichloroethane.

Found %: C 71.56; H 7.26; OH 23.36. $C_{18}H_{22}O_4$. Calculated %: C 71.52; H 7.28; OH 22.50.

Tetracetate. A mixture of 2 g of DL-2,3-(α-hydroxybenzyl)-1,4-butanediol, 8.1 g of acetic anhydride and 0.8 g of freshly-distilled potassium acetate was heated for 1 hour after which it was treated in the same way as that described for meso-2,3-di(α-hydroxybenzyl)-1,4-butanediol tetracetate. 1.2 g of DL-2,3-di-(α-hydroxybenzyl)-1,4-butanediol tetracetate (40%) with m.p. 140-142.5° was obtained. After recrystallizing from alcohol it was in the form of colorless prisms with m.p. 143-143.5°.

Found %: C 66.19; H 6.50. $C_{26}H_{30}O_8$. Calculated %: C 66.38; H 6.38.

3. 2,5-Diphenyl-hexahydro-(3,4 : 3',4')-furofurane (VII). A mixture of 2.32 g of meso-2,3-di-(α-hydroxybenzyl)-1,4-butanediol (m.p. 137-138.5°) and 2 g of anhydrous potassium bisulfate was placed in a Würtz flask connected to a well-cooled receiver. The mixture was heated slowly (for 1 hour) under vacuum (9 mm) and at a water-bath temperature of 110-170°; during this process 0.17 g of water was evaporated off. The remainder was distilled under vacuum (9 mm); the distillate whose main fraction distilled at 220-230° was a yellow syrupy liquid with a pleasant odor, which partially crystallized on the addition of anhydrous ether. The crystals were filtered and dried under vacuum over phosphorus pentoxide. The yield was 0.8 g, the m.p. 87-88.5°. A futher 0.21 g of this substance was obtained by evaporation of the mother liquor. The total yield of 2,5-diphenyl-hexahydro-(3,4 : : 3',4')-furofuran was 54%. It was in the form of long colorless prisms, agglomerating to form star-shaped druses (from anhydrous alcohol) with m.p. 88.5-90°, dissolving readily in benzene, xylene, ethyl acetate, acetone, toluene, chloroform, dichloroethane and carbon tetrachloride; it was rather more difficultly soluble in ether, dioxan glacial acetic acid, ethyl alcohol and petroleum ether; it was insoluble in water.

2,5'-Diphenyl-hexahydro-(3,4 : 3',4')-forufuran does not decolorize a solution of bromine in chloroform or an aqueous solution of potassium permanganate and does not react with Nessler's reagent.

Found %: C 81.09; H 6.69. $C_{18}H_{18}O_2$. Calculated %: C 81.21; H 6.77.

4. 2,5'-Diphenyl-hexahydro-(3,4 : 3',4')-furofuran (IV). A mixture of 2 g of DL-2,3-(α-hydroxybenzyl)--1,4-butanediol (m.p. 147.5-148°) and 1.5 g of aqueous potassium bisulfate was heated slowly (for 1 hour) under vacuum (13 mm) at a water bath temperature of 150-200°. 0.12 g of water was evaporated off. The main part of the substance then distilled over at 13 mm and 220-280° in the form of a viscous orange-red oil with a pleasant odor which on cooling and treatment with anhydrous ether crystallized as fine needles, aggregating in druses. After filtering and drying under vacuum over phosphorus pentoxide 0.36 g of a substance with m.p. 71-73° was obtained. A further 0.09 g of this substance was obtained by evaporation of the mother liquor. The total yield of 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran was 25.6%. It was in the form of colorless needles (from anhydrous alcohol) with m.p. 72.5-74.5°, easily soluble in the usual organic solvents but difficultly soluble in alcohol and insoluble in water; it did not decolorize a solution of bromine in chloroform.

Found %: C 81.29; H 7.04. $C_{18}H_{18}O_2$. Calculated %: C 81.21; H 6.77.

5. Hydrogenation of 2,5-diphenyl-hexahydro-(3,4 : 3',4')-furofuran 1 g of 2,5-diphenyl-hexahydro--(3,4 : 3',4')-furofuran (m.p. 87-88.5°) was hydrogenated over 1.17 g of palladium on charcoal (15% palladium) in 70 cc of glacial acetic acid for 25 hours at room temperature and atmospheric pressure; 220 cc of hydrogen was absorbed (1.98 moles). After separation from the catalyst the acetic acid was removed under vacuum. The residue was diluted with 13 cc of 0.5 N alcoholic caustic soda and warmed on the water bath for 30 minutes. After cooling to 20° the mixture was neutralized with a 15% solution of hydrochloric acid, diluted with water and extracted with ether. The crystals remaining after the evaporation of the ethereal extract were filtered and washed with a small quantity of dry ether. 0.75 g (79%) of 3,4-dibenzyl-tetrahydrofuran with m.p. 60-62° was obtained.

After recrystallizing twice from dilute alcohol the m.p. of the 3,4-dibenzyl-tetrahydrofuran (IX) was 65.5-67°. It was in the form of colorless prisms, aggregating in druses, soluble in the usual organic solvents, difficultly soluble in acetone, alcohol and acetic acid but insoluble in water; it did not give a qualitative reaction for a hydroxyl group with Nessler's reagent.

Found %: C 85.64; H 7.92. $C_{18}H_{20}O$. Calculated %: C 85.71; H 7.94.

6. Hydrogenation of 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofurane. 0.67 g of 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran (m.p. 71-73°) was hydrogenated under the conditions of the previous experiment in the presence of 0.789 g of palladium on charcoal (15% palladium) in 70 cc of glacial acetic acid for 8 hours; 200 cc of hydrogen (1.8 moles) was absorbed. After similar treatment 0.33 g (49%) of DL-2,3-dibenzyl-1,4-butanediol (VIII) with m.p. 84.5-86° was obtained; a sample of this substance in a mixed melt with the substance described below (experiment VII, A and B) did not show a depression of the melting point. It crystallized from ligroin in the form of fine feathery hygroscopic needles with m.p. 87-88°; it was easily soluble in the usual organic solvents and glacial acetic acid but difficultly soluble in carbon tetrachloride, ligroin and water.

Found %: C 80.19; H 7.92; OH 13.07. $C_{18}H_{22}O_2$. Calculated %: C 79.90; H 8.20; OH 12.60.

7. DL-2,3-Dibenzyl-1,4-butanediol (VIII). A. 5 g of DL-dibenzylsuccinic acid [11] (m.p. 172°) in 250 cc of absolute ether was added slowly with stirring to a suspension of 2 g of lithium aluminiumhydride in 50 cc of absolute ether. The reaction mass was mixed for 30 minutes at room temperature and for 6 hours while heated on a water bath. The reaction product was treated in the usual manner. A light-brown viscous oily substance was obtained. By distillation under vacuum at 195-210° (1.6 mm) and continued drying under vacuum 0.18 g (18.3%) of DL-dibenzyl-1,4-butanediol with m.p. 85-86° was obtained. Colorless needles with m.p. 87-88° were obtained from ligroin.

Diethyl ester of DL-2,3-dibenzylsuccinic acid. 2.14 g of DL-2,3-dibenzylsuccinic acid [11] were esterified in the usual manner, heated for 4 hours with 16 cc of anhydrous ethyl alcohol and 1 cc of concentrated sulfuric acid. The yield of the diethyl ester of DL-2,3-dibenzylsuccinic acid was 1.8 g (70.9%). It was in the form of colorless needle-shaped prisms, agregating in druses, with m.p. 80-81.5° (from alcohol); it was soluble in the usual organic solvents and glacial acetic acid but difficultly soluble in alcohol and water. Freudenberg [12] gives an m.p. of 83° for this compound, obtained by a different method.

Found %: C 74.52; H 7.47. $C_{22}H_{26}O_4$. Calculated %: C 74.53; H 7.39.

B. 1 g of diethyl ester of DL-2,3-dibenzylsuccinic acid in 70 cc of absolute ether was added slowly with stirring to a suspension of 0.231 g of lithium aluminiumhydride in 10 cc of absolute ether cooled to 0° so that the temperature of the reaction mass did not exceed 2°. The mixture was stirred for 2 hours at room temperature and for 1 hour with boiling ether. The reaction product was treated in the usual manner. 0.34 g of DL-2,3-dibenzyl-1,4-butanediol (44.6 %) with m.p. 86-88° was obtained. Colorless needles with m.p. 87-88° were obtained from ligroin. Freudenberg [12] gives an m.p. of 70° for this compound, obtained by a different method; it is possible that he obtained the other stereoisomer.

Found %: C 79.82; H 8.17. $C_{18}H_{22}O_2$. Calculated %: C 79.90; H 8.20.

Diacetate. A mixture of 0.28 g of DL-2,3-dibenzyl-1,4-butanediol m.p. 85-87°), 0.95 g of acetic anhydride and 0.09 g of freshly-melted potassium acetate was heated for 1 hours 30 minutes. The reaction mass was treated in the usual manner. 0.18 g (49%) of DL-2,3-dibenzyl-1,4-butanediol diacetate with m.p. 72-73°, was obtained. It was in the form of colorless prisms with m.p. 73.5-74.5° (from alcohol), soluble in the usual organic solvents, difficultly soluble in acetic acid and alcohol and insoluble in water.

Found %: C 74.92; H 7.53. $C_{22}H_{26}O_4$. Calculated %: C 74.53; H 7.40.

8. 2,5-Dinitrophenyl-hexahydro-(3,4 : 3',4')-furofuran 1.22 g of 2,5-diphenyl-hexahydro-(3,4 : 3',4')-furofuran was added in small quantities with stirring for one hour to a mixture of 12.2 g of glacial acetic acid and 6.23 g of nitric acid (d 1.5), the temperature being maintained at about 20°. After keeping for 2 hours the reaction mass was poured on to ice. The blue oily substance which separated out was extracted with ether. After neutralizing with bicarbonate solution and drying over sodium sulfate the ethereal extract was evaporated under vacuum. The viscous oil which remained crystallized on the addition of a small amount of absolute ether. 0.28 g of a substance with m.p. 149-151° was obtained. A further 0.1 g of the same substance was obtained by evaporation of the mother liquor. The total yield of 2,5-di-(nitrophenyl)-hexahydro-(3,4 : 3',4')-furofuran was 17.2%.

It crystallized in the form of small fine needles from alcohol; the m.p. was 156.5-157.5°; it was soluble in chloroform, dichloroethane, carbon tetrachloride, ethyl acetate, benzene, xylene, dioxan ether, difficultly soluble in acetone, ethyl alcohol, glacial acetic acid and ligroin; it was insoluble in a 10 % solution of KOH and in a solution of sodium bicarbonate.

Found %: C 59.93; H 4.88, N 7.54. $C_{18}H_{16}O_6N_2$. Calculated %: C 60.65; H 4.53; N 7.86.

SUMMARY

1. A method for synthesizing substituted hexahydro-(3,4 : 3',4')-furofurans was developed, the example selected being 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofuran ; the racemic dibenzoyl-succinic ester with m.p. 74-78° (Knorr's γ -isomer) which was the starting point of the synthesis was converted to 2,3-di-(α-hydroxybenzyl)--1,4-butanediol and was then subjected to thermal dehydration in the presence of potassium bisulfate.

2. It was shown that, depending on the configuration of the initial debenzoylsuccinic ester and the 2,3-di--(α-hydroxybenzyl)-butanediol obtained by its reduction, dehydration produces either 2,3- or 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofurans.

3. The structure of the isomeric 2,5 and 2,5'-diphenyl-hexahydro-(3,4 : 3',4')-furofurans was proved by their hydrogenation in the presence of palladium on charcoal.

4. From the proof of the structure of the diphenyl-hexahydro-(3,4 : 3',4')-furofurans the conclusion was drawn that Knorr's β -dibenzoylsuccinic ester (m.p. 128-130°) is the meso form and the γ -dibenzoylsuccinic ester (m.p. 74-78°) is the racemate.

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THE INFLUENCE OF LOW-MOLECULAR COMPOUNDS ON THE PHOTOCHEMICAL DESTRUCTION OF POLYSTYRENE

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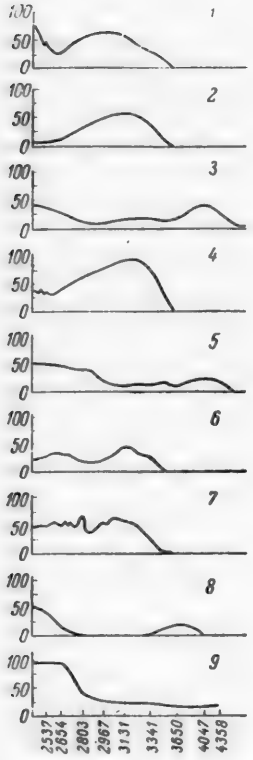

Fig. 1. The absorption spectra of low molecular compounds and polystyrene.
1) Salol. 2) 1,4-Diphenyl--1,3-butadiene, 3) Dixanthylene. 4) β-Methylumbelliferone. 5) 2-hydroxy-1-naphthaldazine. 6) Lepidone. 7) 2-o-Hydroxyphenylbenzoxazole. 8) Diethyl ester of 2,5-dihydroxyterephthalic acid. 9) Polystyrene.
Absorption (as a %) indicated along the ordinate, wavelengths (in A) along the abscissa.

The investigation of the disintegration process of polystyrene under the influence of ultraviolet radiation has been the subject of a number of works [1-4]. The work of Achhammer and other authors established that under the influence of heat and ultraviolet radiation disintegration of the thermolabile polystyrene groups commences, being also accompanied by oxidation if the process takes place in the presence of oxygen; during this process benzene, methylethylketone, dimethylbenzene and alcohol are produced and as a result of oxidation formaldehyde, formic and acetic acids are formed.

The aim of the present investigation was to study the influence of low-molecular organic substances of various structure on the process of the alteration of the properties of polystyrene under the influence of ultraviolet light and, in addition, to find substances able to retard the disintegration of polystyrene under the influence of ultraviolet radiation. For this purpose the spectral analysis of organic substances of various structure was carried out, the substances selected for analysis having their maximum absorption in the ultraviolet part of the spectrum between 270 and 320 mμ, i.e. they approached the region of high-energy wavelengths and corresponded to the region of maximum short-wave absorption of polystyrene.

The following compounds were used as addition agents of this type: 1) salol, 2) β-methylumbelliferone, 3) 2-o-hydroxyphenylbenzoxazole, 4) 1,4-diphenyl-1,3--butadiene, 5) dixanthylene, 6) diethyl ester of 2,5-dihydroxyterephthalic acid, 7) 2-hydroxy-1-naphthaldazine, 8) lepidone.

Fig. 1 gives the absorption spectra of the compounds used and the initial polystyrene.

The addition agents were introduced into the solution of polystyrene before decanting the film, the weight of addition agents used being 1% of that of the polymer. The films containing addition agents of a particular substance were examined under the same conditions as films without these agents. The influence of the total mercury radiation of a PRK-2 lamp and the action of light with a wavelength of 300-320 mμ were investigated separately.

The latter region was investigated because the solar spectrum has a high radiation intensity in the 300-320 mμ region and the relationship of polystyrene films to the action of these wavelengths made it possible to judge the resistance of the polymer to sunlight.

The modifications in the properties of the films which occurred after exposure to light were determined from the change in the molecular weight, the mechanical properties and the absorption spectra in the ultraviolet region.

EXPERIMENTAL

The polystyrene films were prepared by decanting from 10% solution of polystyrene in benzene. The films were dried at room temperature for several days and kept in the dark. The thickness of the films was between 40 and 50 μ. The samples of the films were irradiated in quartz containers situated 50 mm from a PRK-2 mercury-quartz lamp. The lamp was enclosed in a quartz casing, cooled with water, and together with the containers was placed in a glass thermostat, filled with distilled water.

The irradiation of the films by a total light flux from a PRK-2 lamp was carried out in an atmosphere of air for 10 hours at 20°. A longer period of irradiation was not advisable since the samples became brittle and broke when touched. The irradiation of the films with light of a wavelength of 300-320 mμ was carried out for 50 hours at the same temperature. To isolate this region of the spectrum a liquid filter was used to fill the thermostat instead of distilled water. A solution containing 0.044 mole of nickel chloride, 0.0005 mole of potassium bichromate and 0.005 mole of phthalic acid per liter was used as the filter. Under the influence of ultraviolet light the filter was disintegrated in 12 hours and its spectral properties altered. A freshly-prepared filter was used to replace the filter after this period had elapsed.

The irradiated samples of film were tested on a Polyani-type* dynamometer to determine the breaking strengths and breaking elongations.

The ultraviolet absorption spectra were determined on a spectrometer with a high-speed recording photoattachment, constructed in the laboratory by I. V. Obreimov.

DISCUSSION OF RESULTS

Irradiation of polystyrene films with mercury-quartz radiation for 10 hours under the conditions of this investigation leads to disintegration of the polymer. This is shown by the decrease in the breaking strength of the film, the loss of elasticity, the decrease in the molecular weight, the appearance of an insoluble residue and the increase of absorption in the ultraviolet region of the spectrum (Figs. 2-4, Table 1).

The reduction in the molecular weight may take place as a result of the phenomenon, previously noted by one of the authors together with G. S. Kolesnikov and T. A. Soboleva [6], that insoluble trimers are formed primarily by the longest molecules. In consequence, the average molecular weight of the soluble part is reduced.

Ultraviolet radiation with wavelengths of 300-320 mμ has a much weaker influence on polystyrene, as may be seen from the data in Tables 1 and 2.

The influence of organic addition agents on films of polystyrene is indicated in a marked fashion, i. e. by a certain reduction in the breaking strength of the film. Certain compounds, for example, dixanthylene, markedly accelerate the disintegration of the polystyrene by ultraviolet light. This is shown by a considerably greater decrease in the molecular weight, compared with an ordinary polystyrene film, from 44,000 to 8000, an increase in the insoluble residue to 28% and a deterioration in the mechanical properties of the film (Figs. 2,3, Table 1).

The absorption region in the ultraviolet part of the spectrum is markedly increased in the case of the irradiated sample and is displaced towards the long waves (Fig. 4). The structure of the absorption spectrum of the sample acquires diffuse outlines analogous to the structure of the sample of polystyrene without addition agents. The characteristic features introduced by the addition of dixanthylene disappear in the absorption spectrum of the sample.

All the changes found indicate that under the influence of ultraviolet light more fundamental processes of destruction and structuralization of the polymer molecule take place in the polystyrene sample with dixanthylene as the addition agent than in the polystyrene sample without an addition agent. It is also undoubtedly true that the dixanthylene itself disintegrates.

* Transliteration of Russian— Publisher's note.

TABLE 1

Results of Mechanical Tests of Samples of Polystyrene Before and After Irradiation

Sample of polystyrene film	Before irradiation		After 10 hours of irradiation with unfiltered light.		After 50 hours of irradiation with filtered light.	
	Breaking strength σ (kg/ sq.cm)	Breaking elongation E (%).	Breaking strength σ (kg/ sq.cm)	Breaking elongation E (%)	Breaking strenght σ (kg/ sq.cm)	Breaking elongation E (%)
Without addition agents	386	8	242.4	2.36	347	7.4
With salol as addition agent	200	5	218.6	1.4	234	4.9
With 2-o-hydroxyphenylbenzoxazole as addition agent	228	6.95	219.5	1.7	265.5	5.25
With β-methylumbelliferone as addition agent	249.5	5.1	184.3	2.8	255.6	5.7
With 1,4-diphenyl-1,3-butadiene as addition agent	224.5	6.8	236	2.86	301	11.3
With dixanthylene as addition agent.	252	4.5	124.9	1.7	145	3.3
With the diethyl ester of dihydroxyterephthalic acid as addition agent	350	7.5	207.6	2.1	256	3.3
With 2-hydroxy-1-naphthaldazine as addition agent	298	2.8	252.6	0.85	228	7.3
With lepidone as addition agent	621	1.5	307.3	4.2	296	6.3

Note. Rate of breaking of the films 0.0087 mm/ sec.

TABLE 2

Results of Experiments on the Irradiation of Polystyrene Films Containing Various Addition Agent, with Ultraviolet Light with a Wavelength of 300-320 mμ

Addition Agent (1% of the weight of the polymer)	Before irradiation		After irradiation for 50 hours	
	Characteristic viscosity	Molecular weight	Characteristic viscosity	Molecular weight
Without addition agents	0.28	44000	0.28	44000
Salol	0.29	46500	0.29	46500
β-Methylumbelliferone	0.28	44000	0.27	41500
o-Hydroxyphenyl-2-benzoxazole	0.27	41500	0.27	41500
1,4-Diphenyl-1,3-butadiene	0.25	36600	0.25	36600
Dixanthylene	0.27	41500	0.22	29800
Diethyl ester of dihydroxyterephthalic acid	0.27	41500	0.27	41500
o-Hydroxynaphthaldazine	0.25	36600	0.27	41500
Lepidone	0.27	41500	0.26	39000

Note. The molecular weight of the polystyrene was calculated according to the formula $[\eta] = 3.7 \cdot 10^{-4} M^{0.62}$ [5].

Under the influence of irradiation with light with a wavelength of 300-320 mμ the sample of film containing dixanthylene also breaks up, but to a considerably lesser degree. In consequence, the molecular weight of the polymer is reduced from 44,000 to 30,000 (Table 2). During this process the structure of the absorption spectrum shows little change and corresponds to that of the absorption spectrum of the nonirradiated sample of film (Fig. 4).

Under conditions of irradiation with light with a wavelength of 300-320 mμ dixanthylene is evidently not completely disintegrated. This is also confirmed by the residual blue luminescence of the irradiated sample of polystyrene.

The sensitizing influence of dixanthylene is explained by its spectral data. In the long wave region in which there is danger of the polystyrene being disintegrated the absorption spectrum of dixanthylene has a minimum intensity. In addition, under the influence of radiation dixanthylene rapidly disintegrates. It is also extremely probable that the free radicals formed during this process accelerate the destruction of the polystyrene.

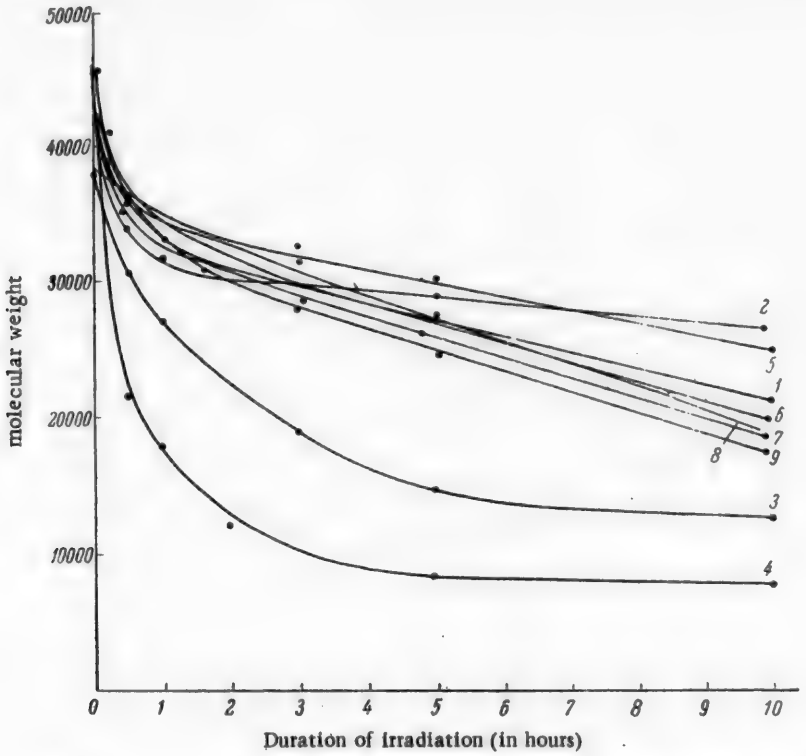

Fig. 2. The reduction of the molecular weight of polystyrene films containing various addition agents, under the influence of irradiation.
1) Polystyrene without addition agents. 2) With 2-hydroxy-1-naphthaldazine as the addition agent. 3) With lepidone as the addition agent. 4) With dixanthylene as the addition agent. 5) With 1,4-diphenyl-1,3-butadiene as the addition agent. 6) With salol as the addition agent. 7) With β-methylumbelliferone as the addition agent. 8) With 2-o-hydroxyphenylbenzoxazole as the addition agent. 9) With the diethyl ester of 2,5-dihydroxyterephthalic acid as the addition agent.

If lepidone is introduced into the polystyrene film the disintegration of the polymer under the influence of ultraviolet light is also accelerated. This is shown by the fall in the molecular weight of the polystyrene to 13,000 and the increase of the absorption zone in the ultraviolet region of the spectrum (Fig. 2). The influence of lepidone on the mechanical properties of polystyrene was very characteristic. A film with this substance as the addition agent shows an increase in strength with a decrease in elasticity. This phenomenon disappears during the process of irradiation and the sample becomes weaker but more elastic, resembling the sample of polystyrene without addition agents (Table 1).

The sensitizing influence of lepidone on the photodestruction of polystyrene is evidently connected with its instability under irradiation. The second reason is possibly the existence of an absorption minimum at 280 mμ in the lepidone spectrum (Fig. 1). The presence of a "dip" of this type in the absorption spectrum of the addition agent facilitates the access of short wave lengths to the polystyrene molecule.

The diethyl ester of 2,5-dihydroxyterephthalic acid has a weak sensitizing influence. The absence of ab-

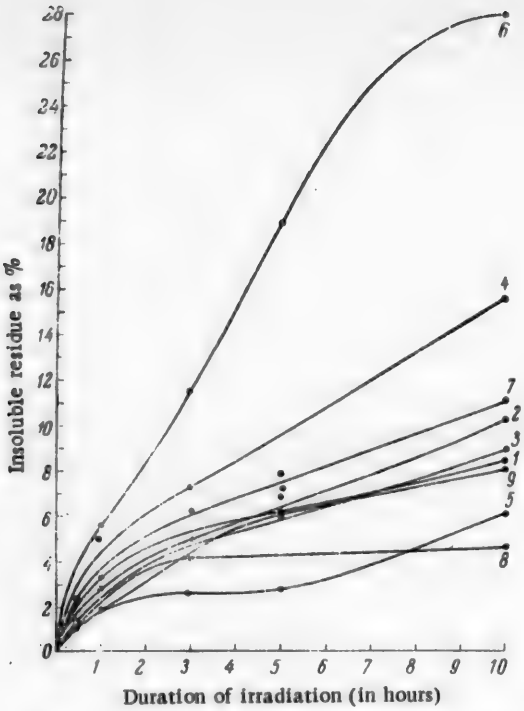

Fig. 3. Increase in the insoluble residue in samples of polystyrene during the process of ultraviolet irradiation.
1) Polystyrene without addition agents. 2) With salol as the addition agent. 3) β-methylumbelliferone as the addition agent. 4) With 2-o-hydroxyphenylbenzoxazole as the addition agent. 5) With 1,4-diphenyl-1,3-butadiene as the addition agent. 6) With dixanthylene as the addition agent. 7) With the diethyl ester of 2,5-dihydroxyterephthalic acid as the addition agent. 8) With 2-hydroxy-1-naphthaldazine as the addition agent. 9) With lepidone as the addition agent.

sorption in its spectrum in the 280-310 mμ region (Fig. 1) may be the explanation of the poor protective action of this compound.

The influence of salol, β-methylumbelliferone and 2-o-hydroxyphenylbenzoxazole was hardly shown during the process of the irradiation of polystyrene films (Fig. 2,3, Table 1). The best results were obtained with salol. β-Methylumbelliferone breaks up slightly during the irradiation process. With this addition agent the absorption spectrum of the irradiated sample corresponds completely to the absorption spectrum of the irradiated polystyrene sample and shows no sign of the presence of β-methylumbelliferone (Fig. 4).

2-o-Hydroxyphenylbenzoxazole assists the structuralization of the polystyrene molecule under the influence of irradiation. Up to 15% of insoluble residue is found in the irradiated sample when this substance is present (Fig. 3).

In spite of the presence of very appropriate spectral data, 2-o-hydroxybenzoxazole and salol (Fig. 1) do not show a sufficient protective influence during the photodestruction of polystyrene.

2-Hydroxy-1-naphthaldazine was found to have certain protective properties. This was shown during the irradiation of a polystyrene sample with light having a wavelength of 300-320 mμ (Figs. 2, 3). In this instance there is a somewhat lesser decrease in the molecular weight, a reduced content of insoluble residue and a rela-

tively slight increase of absorption in the ultraviolet region of the spectrum.

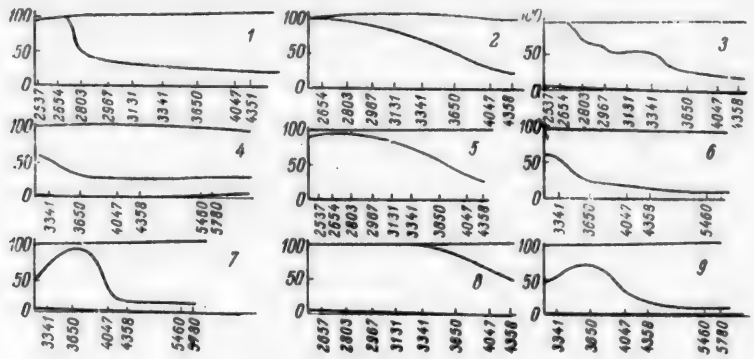

Fig. 4. Absorption spectra of samples of polystyrene.
Polystyrene without addition agents: 1) Before irradiation 2) After irradiation with unfiltered light for 10 hours. 3) After irradiation with filtered light for 100 hours.
Polystyrene with addition of β-methylumbelliferone: 4) Before irradiation. 5) After irradiation with unfiltered light for 10 hours 6) After irradiation with filtered light for 100 hours.
Polystyrene with addition of dixanthylene: 7) Before irradiation. 8) After irradiation with unfiltered light for 10 hours. 9) After irradiation with filtered light for 100 hours.
Absorption (as a %) indicated on the ordinate and wavelength (in A) on the abscissa.

2-Hydroxy-1-naphthaldazine has a group of properties which evidently exerts a favorable influence on the process of the irradiation of polystyrene. This compound has a satisfactory ultraviolet absorption spectrum, exceptional stability under the action of ultraviolet light and luminescent properties which allow a removal, if only partial, of the absorbed light energy in the form of light energy.

1,4-diphenyl-1,3-butadiene showed the best protective properties of all the investigated substances. This was also shown in the case of light with a wavelength of 300-320 mμ. After 50 hours irradiation the polystyrene samples with 1,4-diphenyl-1,3-butadiene as addition agent not only show unimpaired mechanical properties in comparison with nonirradiated samples but even become stronger (Table 1). The decrease in the molecular weight and the insoluble residue content are also less (Figs. 2,3). Absorption in the ultraviolet region of the spectrum is also not increased.

The advantageous effect produced by the addition of 1,4-diphenyl-1,3-butadiene on the irradiated polystyrene film is evidently connected with the fact that the absorption spectrum of 1,4-diphenyl-1,3-butadiene definitely overlaps the long wave region which causes the disintegration of the polystyrene. 1,4-Diphenyl-1,3--butadiene which has considerable stability under the action of ultraviolet light and luminescent properties is evidently a stable filter for the short wave region of the spectrum which causes the disintegration of polystyrene. In addition, part of the energy absorbed by the 1,4-diphenyl-1,3-butadiene, is removed in the form of light.

We found that 1,4-diphenyl-1,3-butadiene has the capacity to retard the polymerization of polystyrene i.e. it shows a certain inhibiting action. To explain this fact styrene was polymerized for 6 hours at 80° both with and without benzoyl peroxide. Hydroquinone, the diethyl ester of 2,5-dihydroxyterephthalic acid, 2-hydroxy-1-naphthaldazine and 1,4-diphenyl-1,3-butadien were also used as addition agents. The results of these investigations are shown in Fig. 5. As may be seen from the data obtained 1,4-diphenyl-1,3-butadiene considerably retards the polymerization reaction of styrene and this is naturally of positive significance during the ultraviolet irradiation of polystyrene. In this instance destruction leads to the formation of free radicals which are associated with inhibitors and thus retards the whole destruction process.

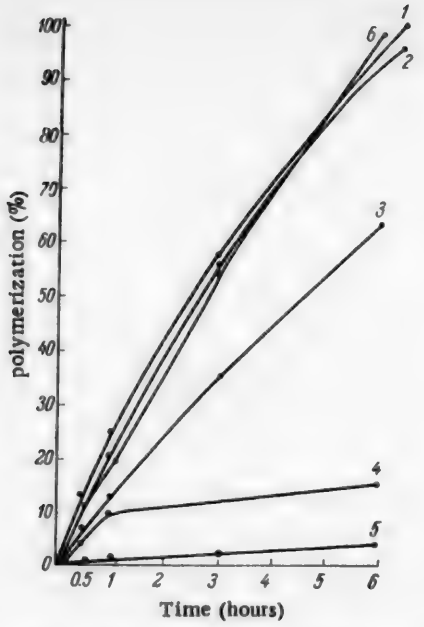

Fig. 5. Polymerization of polystyrene in the presence of low-molecular substances: benzoyl peroxide (1), benzoyl peroxide and diethyl ester of 2,5-dihydroxyterephthalic acid (2), benzoyl peroxide and 1,4-diphenyl--1,3-butadiene (3), benzoyl peroxide and hydroquinone (4), without addition agents (5), benzoyl peroxide and 2-hydroxy-1-naphthaldazine (6).

The authors wish to express their gratitude for the optical and mechanical investigations carried out by I. V. Obreimov, G. L. Slonimsky, I. Ya. Kachkurova and T. A. Dikareva.

SUMMARY

1. The destruction of polystyrene under the influence of ultraviolet light was investigated.

2. It was found that the disintegration of polystyrene is considerably retarded if the total ultraviolet radiation of PRK-2 lamp is replaced by light with a wavelength of 310-320 mμ.

3. It was found that the introduction of low-molecular organic compounds into polystyrene influences the disintegration process. Of the various substances investigated 1,4-diphenyl-1,3-butadiene was found to have the most effective retarding action on the process of the photodestruction of polystyrene.

4. It was shown that the retarding action of the protective addition agent on the rate of destruction of polystyrene evidently depends on the presence of a region of spectral absorption which overlaps the extreme short-wave region of the absorption spectrum of the polymer, the stability of the addition agent itself to ultraviolet light and, in addition, the presence of luminescent properties and an inhibiting action.

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THE REACTION OF ETHYLENE OXIDE AND CYCLOHEXENE OXIDE WITH ORGANOCHLOROSILANES

M. S. Malinovsky and M. K. Romantsevich

Reactions of olefine oxides with organochlorsilanes have not been closely investigated [1, 2]. Sauer and Patnode [1] consider that these reactions proceed in two stages with intermediate formation of halohydrin. In order to investigate these reactions more closely we studied the reaction of ethylene oxide and cyclohexene oxide with organochlorosilanes.

Ethylene oxide and cyclohexene oxide are symmetrical α-oxides and it is, therefore, not necessary to ascertain the direction of rupture of their oxide ring. The structure of the reaction products of these oxides with organochlorosilanes is easily proved by synthesis from the corresponding chlorohydrins and organochlorosilanes. The reaction between ethylene oxide and organochlorosilanes was carried out by passing the oxide into an ethereal solution of chlorosilane, considerable evolution of heat from the reaction mass being noted during this process. In general, ethylene oxide is not absorbed at the commencement of the reaction but, later, when evolution of heat from the reaction mixture takes place a vigorous reaction occurs and ethylene oxide is absorbed. Again, in the instance where the halosilane is first dissolved in ether and the resultant solution heated on a water bath until the ether boils and ethylene oxide then passes through its absorption does not commence until after a certain period of time. The presence of an induction period allows the following conclusions to be drawn with regard to the mechanism of the reaction. In the initial stage the ethylene oxide is converted into glycol chlorohydrin by the action of hydrogen chloride, traces of which are always present in chlorosilanes.

$$H_2C\!-\!CH_2 + HCl \longrightarrow HOCH_2CH_2Cl \qquad (1)$$
$$\quad\ \ O$$

Hydrolysis of the chlorosilane with formation of hydrogen chloride by the action of traces of water in the oxide is also possible. The glycol chlorohydrin then reacts with chlorosilane according to the equation

$$R_nSiCl_{4-n} + (4-n)HOCH_2CH_2Cl \longrightarrow R_nSi(OCH_2CH_2Cl)_{4-n} + (4-n)HCl \qquad (2)$$

Hydrogen chloride is regenerated during this reaction and reacts again with the oxide according to equation (1). When a sufficient amount of hydrogen chloride has accumulated in the reaction mixture the oxide is absorbed.

We synthesized 9 compounds from ethylene oxide and organochlorosilanes, none of which had previously been described in literature. All these compounds were liquids with an estereal odor, insoluble in water and miscible with organic solvents. They were hydrolyzed by water, with particular readiness in the presence of mineral acids. The properties of the synthesized compounds are given in Table 1.

In cyclohexene oxide the carbon atoms of the oxide ring are also the carbon atoms of a cyclohexane ring. We considered it of interest to determine the influence exerted by the unusual structure of this oxide on the addition of chlorosilanes. The condensation cyclohexene oxide with organochlorosilanes was carried out by the slow addition of the oxide to the chlorosilane. By analogy with the above-mentioned mechanism the reactions proceed in two stages

TABLE 1

Compounds Obtained from Ethylene Oxide and Organochlorosilanes

Name of compound	Formulae	Yield (as %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Chlorine (as %)		Silicon (as %)	
						Found	Calculated	Found	Calculated	Found	Calculated
Di-(β-chloroethoxy)-ethylsilane	$(C_2H_5)HSi(OCH_2CH_2Cl)_2$	80.0	66.5—68° (3)	1.4464	1.1523	50.29	51.00	32.60	32.65	12.77	12.93
β-Chloroethoxy-ethyl-N-butylsilane	$(C_2H_5)(н.\text{-}C_4H_9)HSiOCH_2CH_2Cl$	75.7	50 (3)	1.4349	0.9267	54.83	54.66	18.40	18.20	14.27	14.42
Di-(β-chloroethoxy)methyl-chloromethylsilane	$(CH_3)(CH_2Cl)Si(OCH_2CH_2Cl)_2$	79.7	109 (3)	1.4671	1.2671	55.36	55.58	42.16	42.27	11.19	11.16
Di-(β-chloroethoxy)methyl-dichloromethylsilane	$(CH_3)(CHCl_2)Si(OCH_2CH_2Cl)_2$	75.5	117—118 (2.5)	1.4795	1.3454	60.35	60.42	49.64	49.58	9.68	9.82
Tri-(β-chloroethoxy)-ethylsilane	$C_2H_5Si(OCH_2CH_2Cl)_3$	68.3	123—124 (3.5)	1.4597	1.2369	65.43	65.60	36.08	35.98	9.37	9.50
Di-(β-chloroethoxy)-diethylsilane	$(C_2H_5)_2Si(OCH_2CH_2Cl)_2$	75.3	96—97 (4)	1.4526	1.1011	60.14	60.00	28.97	28.92	11.38	11.45
β-Chloroethoxy-ethyl-phenylsilane	$(C_2H_5)(C_6H_5)SiH(OCH_2CH_2Cl)$	67.5	98—99 (3)	1.5043	1.0522	60.46	60.59	16.54	16.51	13.11	13.08
β-Chloroethoxy-dimethyl-propylsilane	$(CH_3)_2(C_3H_7)Si(OCH_2CH_2Cl)$	76.4	71—72 (15)	1.4331	0.9472	49.59	49.59	19.76	19.62	15.34	15.54
β-Chloroethoxy-trimethylsilane	$(CH_3)_3Si(OCH_2CH_2Cl)$	59.2	72—73 (32)	1.4593	1.3814	48.36	48.53	51.99	51.97	—	—

TABLE 2

Compounds Obtained from Cyclohexene Oxide and Organochlorosilanes

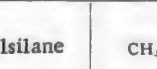
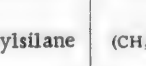
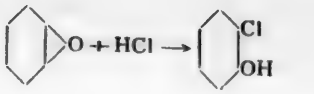
Name of the compound	Formulae	Yield (as %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Chlorine (as %)		Silicon (as %)	
						Found	Calculated	Found	Calculated	Found	Calculated
Tri-(2-chlorocyclohexoxy)-methylsilane		70.3	211—214° (2.5)	1.4971	1.1806	110.0	110.14	24.13	23.96	6.25	6.33
Di-(2-chlorocyclohexoxy)-dimethylsilane		73.4	152—154 (2.5)	1.4844	1.1178	83.32	83.52	21.76	21.80	8.71	8.63

TABLE 2 (Continued)

Name of compound	Formulae	Yield (as %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Chlorine (as %)		Silicon (as %)	
						Found	Calculated	Found	Calculated	Found	Calculated
2-chlorocyclohexoxytrimethylsilane	$(CH_3)_3Si$–O–C$_6$H$_9$Cl	68.7	60—61.5° (3)	1.4565	0.9931	56.36	56.90	17.03	17.15	13.69	13.58
Di-(2-chlorocyclohexoxy)-methylsilane	$(CH_3)HSi(O–C_6H_9Cl)_2$	75.2	156—157 (3)	1.4865	1.1404	78.44	79.15	22.86	22.78	9.15	9.02
Tetra-(2-chlorocyclohexoxy)-silane	$Si(O–C_6H_9Cl)_4$	94.2	T. m. 47—51	—	—	—	—	25.37	25.21	5.18	4.99



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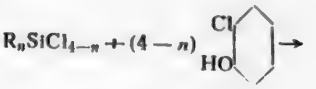

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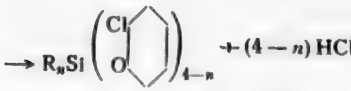
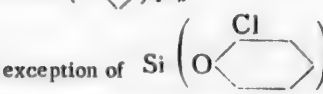


With the exception of  the compounds obtained were liquids with an odor of cyclohexene oxide; they were soluble in organic solvents and insoluble in water. Their properties are given in Table 2.

EXPERIMENTAL

Synthesis of di-(β-chloroethoxy)-ethylsilane. 25.8 g of ethyldichlorosilane and 100 cc of dry ether were placed in a three-necked flask equipped with a mechanical stirrer, reflux condenser, gas pipe and thermometer. Ethylene oxide, previously dried with solid caustic potash was passed into the ethereal solution until absorption ceased. The ether was then distilled off and the residue fractionated under vacuum. 34.7 g (80%) of a liquid which was di-(β-chloroethoxy)-ethylsilane was collected at 66.5-68° (3 mm).

n_D^{20} 1.4464, d_4^{20} 1.1523, MR_D 50.29. $C_6H_{14}O_2Cl_2Si$. Calculated 51.00.

The reaction between other chlorosilanes and ethylene oxide was carried out in a similar fashion.

Synthesis of tri-(2-chlorocyclohexoxy)-methylsilane. 7.47 g of methyltrichlorosilane was placed in the apparatus described above. 14.72 g of cyclohexene oxide was added from a dropping funnel at such a rate that the temperature of the reaction mixture did not exceed 35°. The reaction mixture was then heated for 10 hours at 60-70° and left overlight. The reaction products were distilled under vacuum. 15.6 g (70.3%) of the substance was collected at 211-214° (2.5 mm).

n_D^{20} 1.4971, d_4^{20} 1.1806, MR_D 110.04. $C_{19}H_{33}O_3Cl_3Si$. Calculated 110.14.

The reaction between cyclohexene oxide and other chlorosilanes was carried out in a similar manner.

SUMMARY

1. 9 previously undescribed β-chloroethoxyorganochlorosilanes were obtained by condensing ethylene oxide with certain organochlorosilanes.

2. The addition of organochlorosilanes to cyclohexene oxide was studied for the first time, 5 2-chlorocyclohexoxyorganochlorosilanes being obtained.

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THE INFLUENCE OF THE NATURE OF THE METAL ON THE YIELDS OF ALKANES SYNTHESIZED BY THE WÜRTZ REACTION

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Data on the comparative study of the influence of the nature of the metal and temperature conditions on the yields of the condensation products obtained by the Würtz reaction are almost completely lacking in literature. Examples of the use of other metals used in place of the usual sodium are very rare [1-3]. It was only in the work of one of the authors and his co-workers [4] that it was shown by way of the example of the condensation of two molecules of 3-chloro-2-methyl-1-butene which can undergo an allyl rearrangement that the use of magnesium, sodium and potassium in place of lithium increases the yield of 2,3,4,5-tetramethyl-1,5-hexadiene and reduces the extent of the allyl rearrangement; the allyl rearrangement increases with rising temperature, however, whichever one of these metals is used.

When we were synthesizing isoparaffin hydrocarbons of the series $C_{12}-C_{24}$ we decided to investigate at the same time the influence of the nature of the metal, the temperature conditions and the solvent on the yields of alkanes. Naturally, in this work we could not exclude the influence of the structure of the alkyl halide also and it was, therefore, necessary for us to investigate the influence of the nature of the metal on primary and secondary alkyl halides of various structure.

The investigation of the condensation of the primary alkyl halide, 1-bromo-2-ethylhexane, the results of which are given in Table 1, showed that the yield of alkane increases with a change in the metal used from magnesium to lithium, sodium and potassium. The high yields of 5,8-diethyldodecane, which are as much as 69%, depending on the structure of the alkyl halide ,when sodium is used, can hardly fail to be noted. In this connection it may be pointed out that primary neopentyl- and neohexylchlorides give yields of only 13 and 4.3%, respectively with sodium [5]. When potassium was used our maximum yield of 5,8-diethyldodecane (73 %) was only obtained after replacing ether by isopentane making it possible to exclude secondary reactions with the medium.

TABLE 1

Exp. No.	Metal	Solvent	Temperature of the reaction	Yield of 5,8-diethyldodecane (%)
1	Magnesium	Ether	35°	16.6
2	Lithium	Ether	35	46.4
3	Lithium	Heptane	35	45.6
4	Sodium	Ether	35	68.5
5	Sodium	Isopentane	28	69.1
6	Potassium	Ether	35	59.3
7	Potassium	Ether	20	65.3
8	Potassium	Isopentane	28	72.8

The behavior of three different secondary alkyl halides (4-bromodecane, 2-bromo-3-methylnonane and 3-bromo-2-methyl-5-ethylnonane) during the Würtz synthesis was later studied. All these compounds showed a similar increase in the yields of the corresponding paraffins as a result of a change in the metal used from lithium

to sodium and potassium. The absolute yields were, however, far less because of the considerably greater readiness with which hydrogen bromide was split off. With lithium it was only possible to obtain traces of condensation products but in the case of sodium and potassium their yields varied between 6 and 22 %. It may also be noted that yields of alkanes from 4.3 to 20 % were previously [6] obtained from material condensed by the action of sodium from secondary alkyl halides of different structure.

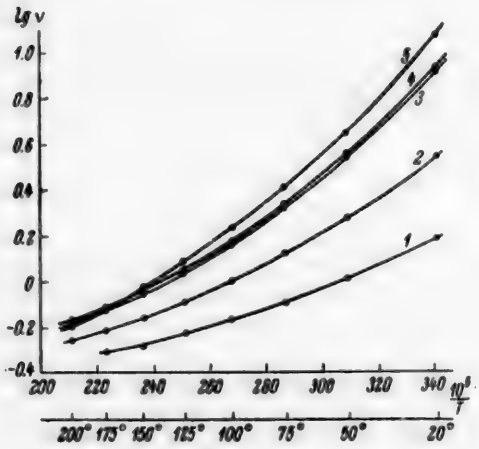

Fig. 1.
1) 2-Methyl-5-ethylnonane. 2) 5,8-diethyldodecane. 3) 7,8-Dipropyltetradecane. 4) 7,8,9,10-tetramethylhexadecane. 5) 5,10-diethyl-7,8-diisopropyltetradecane.

The viscosities of the hydrocarbons obtained are given in Table 2 and Fig. 1. As would be expected, the viscosity of the hydrocarbons increased with increasing molecular weight of the latter; with increasing temperature, however, the difference in the viscosities of paraffins of different composition decreases and at temperatures of 175-200° and over practically disapears. Of the two isomeric eicosanes the more branched 7,8,9,10-tetramethylhexadecane has the higher viscosity.

EXPERIMENTAL

1. Condensation of 1-bromo-2-ethylhexane. The latter was prepared by saturating 2-ethylhexan-1-ol with dry HBr at 120-130° for 12-14 hours:

B. p. 60-61° at 6 mm, n_D^{20} 1.4539, d_4^{20} 1.1092; according to data [7]: b.p. 72-75° at 10 mm, d^{20} 1.086.

All the experiments on the condensation of 1-bromo-2-ethylhexane (except for the experiment with sodium) were carried out in an atmosphere of dry nitrogen according to the following method. 48.3 g (0.25 mole) of 1-bromo-2-ethylhexane was added for a period of 1 hour to 0.5 g-at. of metal (0.25 g-at. in the case of magnesium) in 200 cc of solvent. After stirring for 10 hours at the experimental temperature the reaction mixture was treated in the usual manner; the reaction products were fractionated under vacuum (Table 1).

The hydrocarbon fractions from all the experiments were combined and distilled under vacuum using a fractionating column with an efficiency of 23 theoretical plates, over metallic sodium. A total of 120 g of 5,8-diethyldodecane was obtained:

B. p. 99° at 4 mm, Solidification point -92° (glass), n_D^{20} 1.4373, d_4^{20} 0.7822, MR_D 75.89. Calc. 76.09.

Found %: C 84.81, 84.72; H 15.15, 15.25. $C_{18}H_{34}$ Calculated %: C 84.86; H 15.14.

TABLE 2

Hydrocarbons	Composition	Kinematic viscosity ν (in cSt) at a temperature of:							
		20°	50°	75°	100°	125°	150°	175°	200°
2-Methyl-5-ethylnonane. .	$C_{12}H_{26}$	1.51	1.01	0.79	0.68	0.59	0.52	0.49	—
5,8-Diethyldodecane	$C_{16}H_{34}$	3.49	1.87	1.30	0.99	0.79	0.68	0.60	0.55
7,8-Dipropyltetradecane . .	$C_{20}H_{42}$	8.07	3.43	2.09	1.42	1.08	0.86	0.72	0.65
7,8,9,10-Tetramethylhexadecane	$C_{20}H_{42}$	8.28	3.49	2.15	1.45	1.10	0.90	0.75	0.67
5,10-Diethyl-7,8-diisopropyltetradecane.	$C_{24}H_{50}$	11.46	4.39	2.54	1.70	1.22	0.92	0.74	0.63

2. Condensation of 4-bromodecane. Decan-4-ol was synthesized with a yield of 310 g (75%) by reacting N-hexyl magnesium bromide, obtained from 90 g (3.7 g-at.) of magnesium and 485 g (2.9 moles) of N-hexyl bromide, with 188 g (2.6 moles) of N-butyric aldehyde:

B. p. 96° at 13 mm, n_D^{20} 1.4320, d_4^{20} 0.8262; according to data [8]: b.p. 210-211° at 759 mm, d_0^{20} 0.826.

4-bromodecane with b.p. 97-98° at 11 mm, n_D^{20} 1.4568, d_4^{20} 1.0705, was obtained by the hydrobromination of decan-4-ol at 80°. All experiments were carried out in an atmosphere of dry nitrogen.

Experiment 1. 53.4 g (0.24 mole) of 4-bromodecane was added over a period of 45 minutes to 11.5 g (0.5 g-at.) of sodium at 200 cc of dry benzine (b.p. 100-125°) at 100°, after which this temperature was maintained for a further 4 hours with vigorous stirring. 5.8 g (17%) of 7,8-dipropyltetradecane with b.p. 143-145° at 3 mm, n_D^{20} 1.4442, was obtained by fractionating under vacuum.

Experiment 2. 31 g (0.14 mole) of 4-bromodecane was added (98°, 30 min.) to 7.8 g (0.2 g-at) of potassium in 200 cc of anhydrous N-heptane. 3.7 g (18.6%) of 7,8-dipropyltetradecane, b.p. 111-113° at 1.5 mm, n_D^{20} 1.4440, was obtained from the reaction products.

Experiment 3. 84 g (0.38 mole) of 4-bromodecane was added (25°, 3 hours) to 20 g (0.5 g-at) of potassium in the form of small lumps in 300 cc of absolute ether, after which the reaction mixture was stirred for 12 hours at 35°. 12 g (22.5%) of 7,8-dipropyltetradecane with b.p. 160-161° at 8 mm, n_D^{20} 1.4436, was obtained.

Experiment 4. 30.5 g (0.14 mole) of 4-bromodecane was added over a period of 1 hour to 7.8 g (0.2 g-at) of potassium in 200 cc of absolute ether at temperature of -30°. The reaction mixture was stirred for 10 hours at room temperature and then for a further 4 hours at 35°. 3.9 g (21%) of 7,8-dipropyltetradecane with a b.p. of 164-165° at 9 mm, n_D^{20} 1.4443, was obtained. The hydrocarbon fractions from all the experiments were combined and distilled in a fractionating column with 15 theoretical plates over sodium:

B. p. 161° at 8 mm, solidification point -86° (glass), n_D^{20} 1.4435, d_4^{20} 0.7942, MR_D 94.41; Calc. 94.56.

Found %: C 85.05; 84.92; H 14.89, 15.07. $C_{20}H_{42}$. Calculated %: C 85.01; H 14.99.

3. Condensation of 2-bromo-3-methylnonane. 3-Methyl-2-nonan-2-ol was prepared by a Grignard reaction commencing with secondary octyl magnesium bromide and acetaldehyde(yield 72%).

B. p. 86-88° at 8 mm, n_D^{20} 1.4386, d_4^{20} 0.8353.

Found %: C 76.28, 76.15; H 14.22, 14.02; OH 10.52. $C_{10}H_{22}O$. Calculated %: C 75.88; H 14.01; OH 10.74.

2-Bromo-3-methylnonane was obtained by the treatment of 3-methylnonan-2-ol with dry HBr at 80-100°.

B. p. 74.5-75° at 6 mm, n_D^{20} 1.4586, d_4^{20} 1.0722.

Found %: Br 36.05. $C_{10}H_{21}Br$. Caclulated %: Br 36.13.

Experiment 1. 49 g (0.22 mole) of 2-bromo-3-methylnonane was added (20°, 45 min) to 12.9 g (0.33 g-at) of potassium in 200 cc of absolute ether in a current of dry nitrogen. After stirring, first at 20° (12 hours) and then at 35° (10 hours) 7,8,9,10-tetramethylhexadecane was obtained with a yield of 3.1 g (10%) from the reaction products by repeated distillation over sodium:

B.p. 144-145° at 3 mm, 163-165° at 10 mm, solidification point -88° (glass), n_D^{20} 1.4550, d_4^{20} 0.8112, MR_D 94.50; Calc. 94.56.

Found %: C 85.04, 85.02; H 15.03, 14.93. $C_{20}H_{42}$. Calculated %: C 85.01; H 14.99.

Experiment 2. The repetition of the previous experiment at the boiling point of ether (35°) led to the formation of 7,8,9,10-tetramethylhexadecane with a yield of 7.4 %.

4. Condensation of 3-bromo-2-methyl-5-ethylnonane. 2-methyl-5-ethylnonan-3-ol was obtained with a yield of 128 g (69 %) by a Grignard reaction, commencing with 29.2 g (1.2 g-at) of magnesium, 193.2 g (1 mole) of 1-bromo-2-ethylhexane and 108.2 g (1.5 moles) of isobutyric aldehyde:

B. p. 81-82° at 2.5 mm, n_D^{20} 1.4412, d_4^{20} 0.8471.

Found %: C 77.30, 77.29; H 14.00, 14.05; OH 9.05. $C_{12}H_{26}O$. Calculated %: C 77.35; H 14.07; OH 9.12.

3-Bromo-2-methyl-5-ethylnonane was obtained by treating 2-methyl-5-ethylnonan-3-ol at 100-110° with dry HBr:

B. p. 85° at 2.5 mm, n_D^{20} 1.4578, d_4^{20} 1.0226.

Found %: C 57.86, 57.89; H 10.22, 10.19; Br. 30.26, 30.29. $C_{12}H_{25}Br$. Calculated %: C 57.82; H 10.11; Br 32.07.

Experiment 1. 37.5 g (0.15 mole) of 3-bromo-2-methyl-5-ethylnonane was added at the temperature of the boiling point of ether for a period of 30 minutes to 6.9 g (0.3 g-at) of sodium in 200 cc of absolute ether in a flask filled with dry nitrogen; stirring was then continued for a further 12 hours at 35°. 1.75 g (6.8%) of 5,10-diethyl-7,8-diisopropyltetradecane with a b.p. of 164-166° at 2 mm, n_D^{20} 1.4566, was obtained.

Experiment 2. This was carried out under conditions completely similar to experiment 1, replacing sodium by an equivalent amount of metallic potassium. 2 g (7.8 %) of 5,10-diethyl-7,8-diisopropyltetradecane with b.p. 166-168.5° at 3 mm, n_D^{20} 1.4560, was obtained.

Experiment 3. 41.5 g (0.166 mole) of 3-bromo-2-methyl-5-ethylnonane was added (22°, 1.5 hours) to 13 g (0.33 g-at) of potassium in 200 cc of isopentane in an atmosphere of nitrogen. The reaction mixture was stirred at 22° for 12 hours. 2.7 g (9.6 %) of 5,10-diethyl-7,8-diisopropyltetradecane with b.p. 163-166° at 2 mm, n_D^{20} 1.4563, was obtained by distillation under vacuum. The hydrocarbon fractions from the three experiments were combined and distilled twice under vacuum over sodium:

B. p. 164-166° at 2 mm, solidification point -67° (glass), n_D^{20} 1.4562, d_4^{20} 0.8173, MR_D 112.68; Calc. 113.03.

Found %: C 85.35; H 14.72. $C_{24}H_{50}$. Calculated %: C 85.12; H 14.88.

The disproportionation products consisting of 55-60 % olefin and 40-45% of the paraffin of the composition C_{12}, corresponding in structure to the bromide $C_{12}H_{25}Br$ used in the reaction, were hydrogenated over Raney nickel at 180° and an initial hydrogen pressure of 120 atm for a period of 10 hours. The hydrogenation product was fractionated twice under vacuum over sodium in a fractionating column with 15 theoretical plates. 30 g of 2-methy-5-ethylnonane was isolated:

B. p. 82° at 14.5 mm, solidification point -116° (glass), n_D^{20} 1.4227, d_4^{20} 0.7529, MR_D 57.58; Calc. 57.61.

Found %: C 84.77, 84.62; H 15.28, 15.38. $C_{12}H_{26}$. Calculated %: C 84.61; H 15.39.

SUMMARY

1. A comparative study was made of the influence of the nature of the alkaline metal on the yields of paraffin hydrocarbons in the Würtz reaction. An increase in the yield of hydrocarbon as a result of using lithium, sodium or potassium in place of magnesium was established, the increase being small in the case of secondary alkyl halides and very considerable in the case of primary alkyl halide (1-bromo-2-ethylhexane).

2. A series of hitherto undescribed isoparaffin hydrocarbons was synthesized: 2-methyl-5-ethylnonane, 5,8-diethyldodecane, 7,8-dipropyltetradecane, 7,8,9,10-tetramethylhexadecane and 5,10-diethyl-7,8-diisopropyltetradecane was synthesized and their viscosities studied.

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INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XIX. INVESTIGATION OF THE REACTION BETWEEN β-ARYLGLYCIDIC ACIDS AND AMMONIA AND AROMATIC AMINES

V. F. Martynov and G. Olman

In a number of previous works we established that ethyl esters of β-dialkyl and β-alkylglycidic acids add ammonia, aliphatic and aromatic amines at the β-carbon atom [1-6]. The present work is devoted to an elucidation of the problem of the point where the oxide ring is ruptured in a number of β-arylglycidic acids.

Erlenmeyer (Jr) devoted a number of works to the addition of ammonia and aniline to the sodium salt of β-phenylglycidic acid [7-10]. In his opinion, in this instance the oxide ring is ruptured on the β-carbon-atom side, phenylisoserine or its derivatives being formed. To prove the structure of the product obtained he synthesized phenylserine in the known manner by condensing glycocoll with benzaldehyde and found that the melting points of these two phenylserines were different. On this basis he assumed that the product he obtained was phenylisoserine. He gave no proof at all of the structure of the addition product of ammonia and phenylglycidic acid. Erlenmeyer's experiments on the addition of ammonia to phenylglycidic acid were then repeated by Forster and Rao [11] who came to the opposite conclusion, considering that in this instance the oxide ring is ruptured on the α-carbon atom side with the formation of phenylserine. To prove the structure of the product obtained they synthesized phenylserine by the known method and found that both products were identical. The melting point of the phenylserine which they obtained did not coincide, however, with the melting point of Erlenmeyer's phenylserine and they assumed that they had obtained the other diastereoisomer.

By reacting β-phenyl-β-hydroxy-α-haloidpropionic acid with ammonia Österlin [12] obtained a compound which when oxidized by potassium permanganate in dilute sulfuric acid gave phenylaminoacetic acid. From this he assumed that he had obtained phenylisoserine. It must be pointed out that this compound can only be obtained via the intermediate formation of β-phenylglycidic acid. By carrying out the experiment by reacting ammonia with phenylglycidic acid he obtained a compound, however, which under the same oxidation conditions was decomposed into benzaldehyde and ammonia, i.e. it behaved as if it had the structure of phenylserine.

Generalizing on the basis of the available data in literature and their own experimental results on the addition of ammonia, aliphatic and aromatic amines to the ethyl ester of β-phenylglycidic acid Fourneau and Billeter [13] came to the conclusion that ammonia and aliphatic amines are added at the β-carbon atom while aromatic amines are added at the α-carbon atom. The method they employed for a proof was catalytic reduction over palladium, as a result of which hydroxyphenylpropionic acid was obtained. With deamidization of the addition product with aniline they obtained β-hydroxy-β-phenylpropionic acid but in the case of the addition product with dimethylamine they obtained α-hydroxy-β-phenylpropionic acid.

Information in literature on the reaction of other β-monoarylglycidic acids with amines is very scanty. For example, Rosenmund and Dornsaft [15] tried to add ammonia to the ethyl ester of p-methoxyphenylglycidic acids in order to obtain p-methoxyphenylserine. They only succeeded, however, in obtaining traces of the main product.

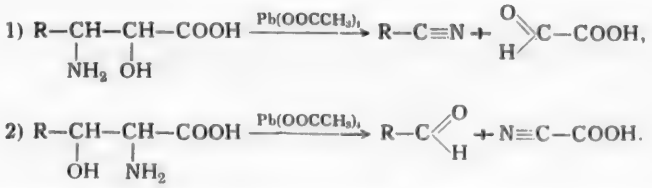
From the brief review above it is evident that the data of authors regarding the point where the oxide ring in β-phenylglycidic acids is ruptured are contradictory. This is explained by the fact that the majority of the

authors based their proof of the structure of the products obtained on the comparison of their melting points with similar compounds obtained by different methods. This type of proof cannot be considered as conclusive, however, because in the case of the addition of amines to β-phenylglycidic acid isomers can be formed not only as a result of a difference in the rupture of the oxide ring but also by the presence of two asymmetric carbon atoms which can lead to the formation of two diastereoisomeric forms for each addition product. The proof of the structure of certain products given in Fourneau and Billeter's article is more conclusive. However, the general conclusion of the French scientists that ammonia and aliphatic amines, on the one hand, and aromatic amines, on the other hand, rupture the oxide ring of β-phenylglycidic acid in different ways does not appear very convincing to us.

The point is that in our previous work with β-monoalkyl- and β-dialkylglycidic acids [1-6] no difference was found in the action of the above-mentioned amines. This fact is quite understandable since both aliphatic and aromatic amines are nucleophyllic agents differing only quantitatively in the degree of their basicity.

With this in mind we decided to again investigate the addition of ammonia and aniline to β-phenylglycidic acid.

In order to prove Fourneau and Billeter's law in the case of the addition product of ammonia with the ethyl ester of β-phenylglycidic acid we used the lead tetraacetate method for oxidizing this compound. This method is based on the fact that as a result of the action of the lead tetraacetate the bond between the carbon atoms containing the amine and hydroxyl groups is broken. At the same time, depending on the structure of the initial compound, the following products are formed:



When we oxidized hydroxyamino-β-phenylpropionamide we obtained only benzaldehyde. In consequence, the addition product of ammonia and the ethyl ester of β-phenylglycidic acid must be assumed to have the structure of β-hydroxy-α-amino-β-phenylpropionamide.

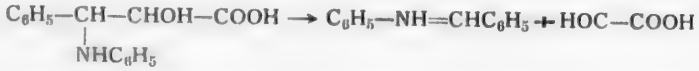
We, therefore, proved that despite Fourneau and Billeter's assertion ammonia is added to the ester of β--phenylglycidic acid at the α-carbon atom.

Unfortunately all our attempts to add ammonia to the sodium salt of phenylglycidic acid, according to Erlenmeyer's method [10], were unsuccessful. The resultant acid obtained did not contain nitrogen.

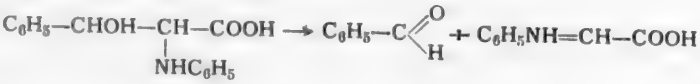
As regards the structure of the addition product of aniline and the ethyl ester of β-phenylglycidic acid we made a further investigation of this compound because contrasting data had been given by various authors. Taking into consideration that these authors used different initial compounds (sodium salt of phenylglycidic acid, the ethyl ester of phenylglycidic acid, β-phenyl-α-haloid-β-hydroxypropionic acid) and bearing in mind the possibility of the influence of a slight alteration of the electronic configurations of the initial substances during the course of the reaction we reacted aniline with all the compounds listed above. It was found that the same product was obtained in each instance. This result confirms the assumption of other authors [11, 13, 14] that the replacement of chlorine in β-phenyl-β-chlor-α-hydroxypropionic acid proceeds via the intermediate closure of the oxide ring and the point of the addition of aniline is determined by the laws governing breaking of the ring.

We subjected the addition product of aniline and β-phenylglycidic acid which we obtained to the action of concentrated sulfuric acid during heating. If the aniline was added to the β-carbon atom, in the reaction we earlier discovered we should have obtained 2-phenylindole. When the reaction was carried out repeatedly, however, we did not once succeed in finding traces of indole; tar was formed on each occasion and the initial product was partially restored. This result of our experiments could only be explained by the fact that aniline is added to the α-carbon atom, i.e. in agreement with Fourneau and Billeter's data. Like all β-hydroxy acids the β-hydroxy--α-anilino-β-phenylpropionic acid formed readily splits off water, being converted into the unsaturated acid which becomes tarry in a medium of sulfuric acid (at 110-115°).

It was of interest to investigate the manner in which lead tetraacetate acts on β-hydroxy-α-anilino-β--phenylpropionic acid. From the structure of this compound the formation of benzaldehyde might have been expected. When oxidized, however, we obtained benzalaniline instead of benzaldehyde. The impression was obtained that aniline adds at the β-carbon atom, not at the α-carbon atom.

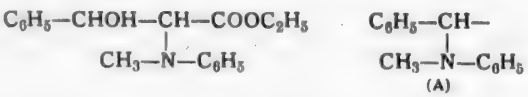


This result which at first sight is in contrast to all the facts previously obtained can, however, be explained in the following manner: on oxidation β-hydroxy-α-anilino-β-phenylpropionic acid should form benzaldehyde and phenyliminoacetic acid,

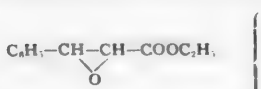
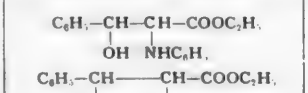
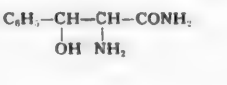
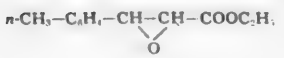
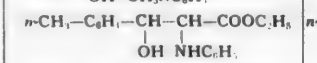
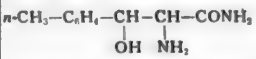
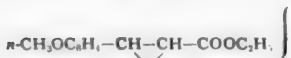
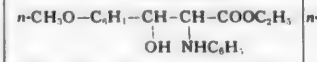
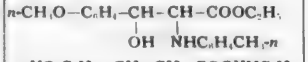
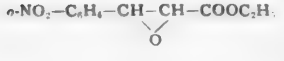
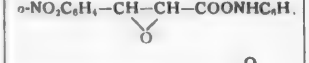
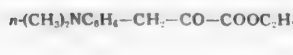
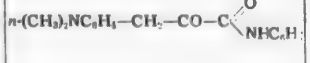


which in the free state is unstable and is converted into diaminostilbenedicarbonic acid [17]. This conversion is connected with the breaking of the -NH=CH- bond and it is quite probable that the radical gives benzalaniline when it reacts with the benzaldehyde.

To prove this we oxidized the addition product of methylaniline and β-phenylglycidic ester. Methylaniline must add in the same way as aniline; we could, therefore, attribute the formula of the ethyl ester of β-hydroxy--α-methylanilino-β-phenylpropionic acid to the compound obtained.



When this compound was oxidized we obtained only benzaldehyde; in actual fact, therefore, methylaniline adds at the α-carbon atom. If the benzaldehyde was formed as a result of further splitting off of the fraction (A) we should have found methylaniline in the distillate of the reaction mixture. It was not found, however. It is clear that without verification of this type this method does not give coinciding results.

Glycidic esters	Reaction products	
	With aromatic amines	With ammonia
		
		
		
		
		
		

To identify the products which we obtained we made use of information given in literature that N-acylamino-hydroxy acids are not oxidized by lead tetracetate under these conditions. If oxidation did nevertheless take place in a case of this type it would only be as a result of the proximity of the hydroxy and carboxylic groups. Unfortunately, all attempts to acetylate the compounds we obtained, even freshly-prepared ketene, were not successful. The results we obtained nevertheless confirmed the correctnes of Fourneau and Billeter's conclusion that when reacted with phenylglycidic acid aromatic amines add at the α-carbon atom.

We devoted the next part of our work to an explanation of the influence of substituents in the phenyl ring of glycidic acid at the point where the oxide ring is ruptured when reacted with ammonia and aromatic amines. Since we had previously established that in the corresponding glycidic acids aliphatic radicals direct the attacking groups into the β-position we considered that by analogy with aliphatic glycidic esters in arylglycidic esters, with substituents which act in the same way as alkyl groups, i.e. give electrons, the oxide ring is ruptured on the β-carbon atom side.

With this in mind we obtained the ethyl esters of (p-methyl)- and (p-methoxy)-β-phenylglycidic acids and studied their interaction with ammonia and aromatic amines. When converted from phenylglycidic acid to p--methylphenylglicidic acid the yield of the reaction product with ammonia falls sharply (16%), while on the other hand the yield of the tarry product increases. No addition product at all was found with ammonia in the case of p-methoxyphenylglycidic acid and only glycidamide and a considerable amount of tar were obtained. When the addition product of ammonia and p-methylphenylglycidic acid was oxidized with leadtetracetate the only product was p-toluyl aldehyde which indicates that in this case also, the oxide ring was ruptured on the α-carbon atom side.

The low yield of β-hydroxy-α-amino-β-phenylpropionamide may be explained by the low stability of this compound. The presence of an electron-donor group in it must make the hydroxyl group still more mobile. The probability of this explanation is confirmed by the fact that in the case of p-methoxyphenylglycidic acid no addition product at all was obtained with ammonia. The methoxy group which is a more active source of electrons evidently makes the existence of the corresponding β-hydroxy-α-amino-β-phenylpropionamide impossible.

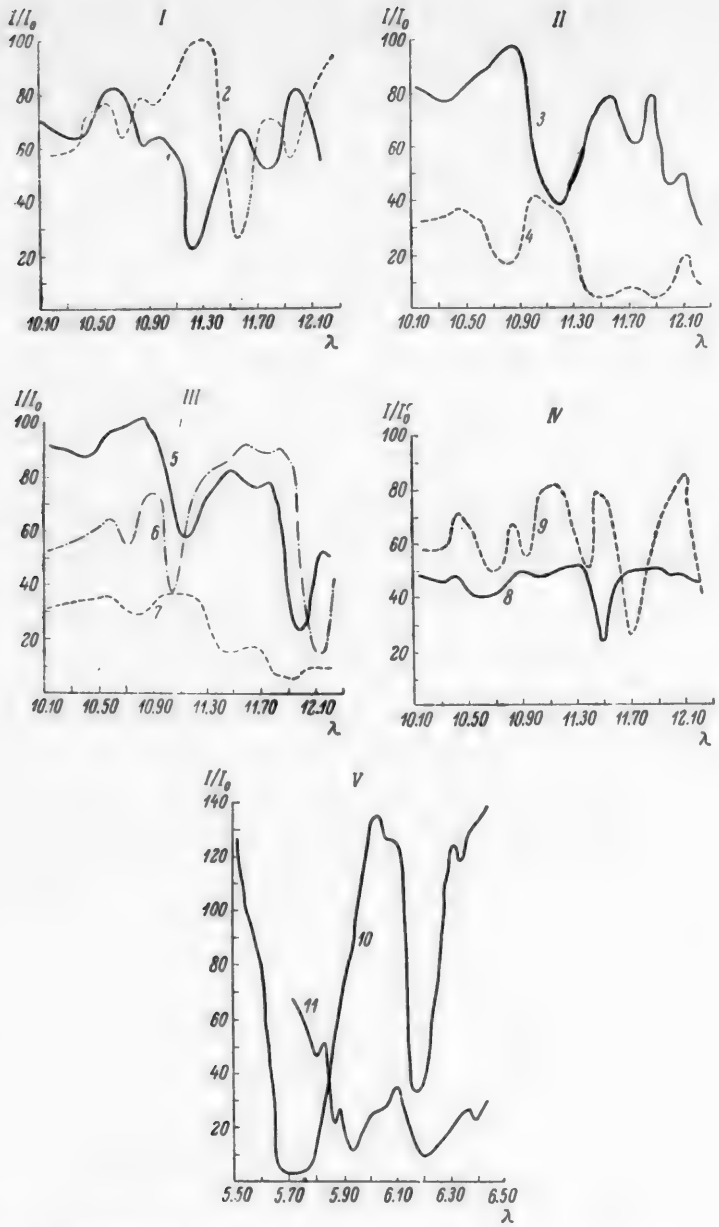
After the reaction of these esters with aromatic amines which, as is known, have less marked basic properties, the corresponding addition products were obtained with the usual yields found in these instances. Their formulae are given in Table 1. When they were acted on by concentrated sulfuric acid they were not converted into indoles. In the case of hydroxy-anilino-p-toluylpropionic acid, apart from tar only the sulfonated initial product was obtained from the reaction mixture. With similar treatment hydroxyanilino-p-methoxyphenylpropionic acid also gave tar. These data justify our assertion that the oxide ring of these glycidic acids is ruptured on the α-carbon atom side.

In order to complete the data obtained we tried to obtain the ethyl ester of p-dimethylaminophenylglycidic acid by condensing p-dimethylaminobenzaldehyde with the ethyl ester of chloroacetic acid. As a result of the reaction we obtained a compound corresponding by analysis to the above-mentioned glycidic acid. When the reaction was carried out with aniline, however, a product was obtained which corresponded by analysis to an anilide, not to an addition product. In this connection, to prove the structure it was necessary to use the method of infrared spectra. In order to draw correct conclusions the spectra of the glycidic esters obtained and their addition products were determined. It was found that the only characteristic absorption maximum for the oxide ring in the region of wavelengths investigated by us is in the 893-903 cm^{-1} range. From comparison with the spectra of the addition products it is evident that the rupture of the oxide ring is associated with the disappearance of this same maximum (Figs. I-V).

The characteristic maximum for the oxide ring is absent in the spectra of the presumed ethyl ester of p--dimethylaminophenylglycidic acid but, in addition to the characteristic absorption distinctive of an estereal carbonyl group (1726 cm^{-1}), the deep trough of a ketonic carbonyl group (1689 cm^{-1}) appears. A completely similar picture is also found in the spectrum of its addition product with aniline (Figs. IV and V). On this basis we must attribute the structure of the corresponding keto acid to the product we obtained.

It is known [18] that the ethyl ester of β,β'-diphenylglycidic acid isomerizes during distillation into the ester of β,β'-diphenylpyroracemic acid. By analogy with this closely-studied case we can attribute the structure of the ethyl ester of p-dimethylaminophenylpyroracemic acid to our product.

On the basis of the above the conclusion can obviously be drawn that substituents which have a very marked

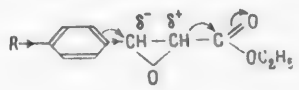


Figs. I-V. Spectra in the infrared region

1) Ethyl ester of β-phenylglycidic acid. 2) Ethyl ester of β-phenyl-β-hydroxy-α--anilinopropionic acid. 3) Ethyl ester of β-(p-methylphenyl)-glycidic acid. 4) Ethyl ester of β-(p-methylphenyl)-β- hydroxy-α-anilinopropionic acid. 5) Ethyl ester of β-(p-methoxyphenyl)-glycidic acid. 6) β-(p-methoxyphenyl)--glycidamide. 7) Ethyl ester of β-(p-methoxyphenyl)-β-hydroxy-α-anilinopropionic acid. 8) Ethyl ester of β-(p-dimethylamino)-pyroracemic acid. 9) Anilide of β-(p-dimethyl-aminophenyl)-pyroracemic acid. 10) Ethyl ester of β-phenylglycidic acid. 11) Ethyl ester of β-(p-dimethylaminophenyl)-pyroracemic acid.

capacity to donate electrons make the oxide ring in glycidic acids less stable. In this sense the dimethylamino group has a more powerful action than two phenyl rings.

As a result of the work carried out by us it was established that, like phenylglycidic ester itself, all phenylglycidic ester, replaced by electron-donor substituents in the phenyl ring add ammonia and aromatic amines at the α-carbon atom. This phenomenon is evidently connected wiht the strong extinction, clearly shown in alkylglycidic esters, of the positive charge at the β-carbon atom.



As a result of this, addition in the α-position is made easier.

EXPERIMENTAL

The synthesis of the ethyl ester of β-phenylglycidic acid was carried out by Darzens' method [19, 20]. Sodium ethylate (1 mole) was added in small portions to a mixture of 106 g (1 mole) or reshly-distilled benzaldehyde, 122 g of the ethyl ester of monochloroacetic acid and 500 cc of absolute ether with stirring and cooling to -10°. During this process the temperature did not rise above 0°. After the addition of all the sodium ethylate the mixture was dissolved in water and the ethereal and aqueous layers were separated from each other. After standing for a short time the sodium salt of phenylglycidic acid, which is difficultly soluble in water, separated out from the aqueous layer. The glycidic ester distilled in the 110-112° range (0.5 mm). 90 g of phenylglycidic ester and 25 g of the sodium salt of β-phenylglycidic acid were obtained the total yield was 60%.

Synthesis of β-hydroxy-α-amino-β-phenylpropionamide. A solution of 20 g of the ethyl ester of phenylglycidic acid in 35 cc of ethyl alcohol (96%) was saturated at 0° with ammonia after which it was sealed in an ampoule and left for 20 days at room temperature. The colorless crystals which precipitated out were separated and heated for 5 hours with a concentrated aqueous-ammonia solution on a water bath. After this the product obtained was recrystallized twice from hot water. 10 g was (53%) obtained. The m.p. was 188-190°.

Found %: N 15.71. $C_9H_{12}O_2N_2$. Calculated %: N 15.55.

Synthesis of the ethyl ester of β-hydroxy-α-anilino-β-phenylpropionic acid. A mixture of 20 g of the ethyl ester of β-phenylglycidic acid, 15 g of aniline and 35 ml of ethyl alcohol was heated to boiling in a reflux condenser for 14 hours. After removing the alcohol and aniline excess in the interval of 165-170° (0.5 mm), ethyl β-hydroxy-α-anilino-β-phenylpropionic acid was distilled over and had the appearance of very thick, yellow butter. 18 g (61 %) of product was obtained which on standing slowly began to crystallize; addition of 1 drop of benzene brought about rapid crystallization. After two recrystallizations from benzene the product had m.p. 73-74°. Saponification of the ester with alcoholic alkali produced the sodium salt, which, when reacted with acetic acid, yielded the free acid. After recrystallization from aqueous alcohol, the substance obtained was in the form of white, fluffy needles. M. p. 163-164°.

Found %: N 5.46. $C_{15}H_{15}O_3N$. Calculated %: N 5.4.

Synthesis of the ethyl ester of β-hydroxy-α-anilino-β-phenylpropionic acid. A mixture of 15 g of the sodium salt of β-phenylglycidic acid, 15 g of aniline and 80 cc of 50 % ethyl alcohol was heated to boiling in a flask with a reflux condenser for 10 hours. The excess aniline was steam distilled. The sodium salt of the addition product was washed several times with ether after which it was dissolved in water. After acidification of the aqueous solution with acetic acid, white crystals were immediately precipitated. After recrystallizing from aqueous alcohol the m.p. was 163-164°. A mixed melt with the acid obtained from the ethyl ester of β-phenylglycidic acid showed no depression of the melting point.

Synthesis of the ethyl ester of β-hydroxy-α-anilino-β-phenylpropionic acid from the ethyl ester of α-hydroxy-β-chlor-β-phenylpropionic acid. A mixture of 8.5 g of the ethyl ester of α-hydroxy-β-chlor-β-phenylpropionic acid, 14 g of aniline and 30 cc of 96 % ethyl alcohol was heated for 5 hours at 130° in a sealed ampoule. After distillation of the alcohol a brown crystalline mass remained. In order to remove hydrogen chloride from the hydrochloride of the addition product it was suspended in absolute ether and a current of dry ammonia passed through the suspension for half an hour. The solid residue of salt was filtered off and the ether and excess aniline were distilled. At a pressure of 0.5 mm a thick yellow liquid distilled in the 168-170° range and after long standing crystallized out. After recrystallizing twice from benzene the m.p. of the product was 73-74°. 7.5 g (71 %) was obtained. A mixed melt with the product obtained from phenylglycidic ester showed no depression of the melting point.

Synthesis of the ethyl ester of β-hydroxy-α-methylanilino-β-phenylpropionic acid. A mixture of 10 g of the ethyl ester of β-phenylglycidic acid and 16.5 g of methylaniline was heated for 9 hours at 130-135° in a sealed ampoule. A thick liquid distilled over in the 170-173° under a vacuum of 0.5 mm. It crystallized out very slowly on standing; the addition of a drop of benzene accelerated crystallization. The yield was 10 g (77 %). After recrystallizing twice from aqueous alcohol the substance had an m.p. of 80-81°.

Found %: N 4.88. $C_{18}H_{21}O_3N$. Calculated %: N 4.68.

Attempt at the addition of ammonia to the sodium salt of β-phenylglycidic acid. 10 g of the sodium salt of phenylglycidic acid was dissolved in 80 cc of an aqueous solution of ammonia, saturated at 0°, and the reaction mixture was allowed to stand at room temperature for 3 weeks. After the ammonia and part of the water had been removed by distillation the solution was acidified with acetic acid; a white crystalline precipitate was formed after this addition of acid. After recrystallizing from aqueous alcohol colorless needle-shaped crystals were obtained with m.p. 132-133°. The yield was 3 g. The substance did not contain nitrogen.

Found %: C 64.79; H 3.58

Oxidation of β-hydroxy-α-amino-β-phenylpropionamide by lead tetracetate. 14.6 g of lead tetracetate was added to a solution of 3 g of the amide in 50 cc of glacial acetic acid. The reaction mixture was heated for 3 hours to 50°. After adding 20 cc of water the reaction mixture was neutralized with alkali and steam distilled. A colorless oil with an odor of bitter almonds was collected in the receiver. The complex with dimedon had an m.p. of 194-195°. A mixed melt of this complex with a sample of the complex obtained from benzaldehyde and dimedon showed no depression of the melting point. The product obtained after oxidation of 3 g of the amide was treated with phenylhydrazine, 2.25 g (70 %) of benzaldehyde phenylhydrazone with m.p. 154-155° being obtained. A mixed melt with the known phenylhydrazone did not show any depression of the melting point (153-154°), which agrees with the data in literature [21].

Oxidation of the ethyl ester of β-hydroxy-α-anilino-β-phenylpropionic acid by lead tetracetate. 1 g of the ethyl ester of β-hydroxy-α-anilino-β-phenylpropionic acid and 1.5 g of lead tetracetate were dissolved in 25 cc of glacial acetic acid. The reaction mixture was left at room temperature for 2.5 hours; during this period it darkened considerably. After treatment in the manner described above 0.2 g of a crystalline substance, which after reapeated steam distillation had an m.p. of 47-48°, was obtained. A mixed melt with known benzalaniline (m.p. 48°) showed no depression of the melting point.

Oxidation of the ethyl ester of β-hydroxy-α-methylanilino-β-phenylpropionic acid by lead tetracetate. The oxidation reaction was carried out in exactly the same manner as in the previous instance. 1 g of the investigated substance and 1.5 g of lead tetracetate were dissolved in 20 cc of glacial acetic acid. After similar treatment an oil with an odor of bitter almonds was collected in the distillate. After the addition of phenylhydrazine it was completely converted into a crystalline precipitate. After recrystallizing from alcohol it had an m.p. of 154-155°.

The action of concentrated sulfuric acid on the sodium salt of β-hydroxy-α-anilino-β-phenylpropionic acid. 5 g of the sodium salt was heated with constant stirring with 10 cc of concentrated sulfuric acid at 110-115°. During this process the reaction mixture darkened considerably. After heating for 30 minutes the mixture was poured into cold water; a black tar separated out and was filtered off. When neutralized slowly with caustic soda solution a white crystalline precipitate was deposited from the still acid filtrate. It was filtered off and recrystallized from aqueous alcohol. Needle-shaped crystals which showed no depression of the melting point in a mixed melt with β-hydroxy-α-anilino-β-phenylpropionic acid were obtained.

The synthesis of the ethyl ester of (p-methylphenyl)-glycidic acid [22] was carried out by Darzens' method. 70 g (62 %) of the ester was obtained from 68 g of p-toluylaldehyde, 65 g of the ethyl ester of monochloroacetic acid and 34 g of sodium ethylate. The b.p. was 119-123° (0.5 mm).

Synthesis of the ethyl ester of β-hydroxy-α-anilino-β-(p-methylphenyl)-glycidic acid. A mixture of 10 g of glycidic ester and 13.5 g (1 : 3) of aniline was heated in a sealed ampoule for 6 hours at 130-150°. After distillation of the excess aniline and unreacted glycidic ester a thick yellow liquid distilled over at 160-165° and 0.5 mm. After redistillation it distilled in the 165-167° range. 7.9 g (55 %) was obtained. The product obtained did not crystallize out, even on long standing; rapid crystallization only resulted after the addition of a few drops of benzene. After recrystallization from benzine it had an m.p. of 69-70°.

Found %: N 4.72. $C_{18}H_{21}O_3N$. Calculated %: N 4.67.

Synthesis of β-hydroxy-α-amino-β-(p-methylphenyl)-propionamide. A solution of 10 g of the ethyl ester of p-methylphenylglycidic acid in 15 cc of 96 % ethyl alcohol was saturated with dry ammonia in an ampoule at 0°. The ampoule was sealed and heated for 5 hours on a water bath. After 2 days a white crystalline precipitate (1.5 g, 16%) came out of solution after the ammonia had first been removed. After recrystallizing from aqueous alcohol it had an m.p. of 168°.

Found %: N 14.51 $C_{10}H_{14}O_2N_2$. Calculated %: N 14.42.

The oxidation of β-hydroxy-α-amino-β-(p-methylphenyl)-propionamide by lead tetracetate was carried out in a similar manner to the examples described above. 0.5 g of amide and 2.3 g of lead tetraacetate were used for the reaction. When steam distilled a slightly yellowish oily product collected in the distillate. It was extracted with ether and distilled from a small flask. At 195° 3 drops of a liquid with n_D^{16} 1.5431 (the value of n_D^{20} for p-toluylaldehyde is 1.5478) distilled over. A phenylhydrazone which crystallized from alcohol in the form of yellowish leaflets and had an m.p. of 108° was obtained (two values are given in literature for the m.p. of p-toluylaldehyde phenylhydrazone, 108 and 121°).

The action of concentrated sulfuric acid on the ethyl ester of β-hydroxy-α-anilino-β-(p-methylphenyl)-propionic acid. 5 g of the product was heated in a small flask with concentrated sulfuric acid for 20-30 minutes at 110-115°. The contents of the flask were then poured into cold water. After neutralization of the aqueous solution with caustic alkali it became transparent and after standing for some time sodium sulfate was deposited. The aqueous solution was separated from the crystalline precipitate and left for 24 hours. During this period a very finely-crystalline precipitate of an organic substance was formed.

Found %: N 3.51; S 8.00. $C_{16}H_{15}O_6NSNa_2$. Calculated %: N 3.54; S 8.08.

Synthesis of the ethyl ester of β-(p-methoxyphenyl)-glycidic acid. 105 g (50 %) of the ester was obtained by the above-described Darzens' method from 136 g (1 mole) of anisaldehyde (freshly-distilled) and 123 g of the ethyl ester of monochloracetic acid dissolved in 700 cc of absolute ether and 68 g of sodium ethylate. The b.p. was 157-158° (0.5 mm).

Synthesis of the ethyl ester β-hydroxy-α-anilino-β-(p-methoxyphenyl)-propionic acid. 15 g of glycidic ester and 19 g of aniline were heated in a sealed ampoule for 5 hours. After this the reaction mixture was distilled at 0.5 mm. A very thick yellow liquid distilled over in the 190-193° range. 10 g (50 %) was obtained.

n_D^{20} 1.5915, d_4^{20} 1.1783, MR_D 87.09; Calc. 88.40; EM_D 1.30.

Found %: N 4.50. $C_{18}H_{21}O_4N$. Calculated %: N 4.45.

Attempt to add ammonia to the ethyl ester of β-(p-methoxyphenyl)-glycidic acid. 10 g of the glycidic ester was dissolved in 25 cc of a saturated aqueous solution of ammonia and heated in a sealed ampoule on a water bath for 4 hours. Crystals were deposited when the reaction mixture was cooled. After the alcohol had been partially removed by distillation a further number of crystals were deposited. After complete removal of the alcohol a tarry mass, which did not form a salt with dry hydrogen chloride, remained in the flask. After recrystallizing twice from aqueous alcohol the crystals obtained had an m.p. of 151°. The substance was not oxidized by lead tetracetate and showed an absorption maximum, characteristic of an oxide ring, in the infrared spectrum.

Found %: N 7.40. $C_{10}H_{11}O_3N$. Calculated %: N 7.26.

Synthesis of the ethyl ester of β-hydroxy-α-(p-toluidino)-(p-methoxyphenyl)-propionic acid. An alcoholic solution of 10 g of glycidic ester and 10 g of p-toluidine was heated in a sealed ampoule for 5 hours at 130-135°. After the alcohol and excess p-toluidine had been distilled off a very thick yellow liquid, which crystallized out after standing for a certain period, distilled over in the 195-203° range at 0.5 mm. 5 g (35 %) was obtained. After recrystallizing twice from petroleum ether the substance had an m.p. of 97-98°.

Found %: N 4.53. $C_{19}H_{23}O_4N$. Calculated %: N 4.25.

The synthesis of the ethyl ester of (p-dimethylaminophenyl)-pyroracemic acid was carried out by Darzens' method. 54 g of p-dimethylaminobenzaldehyde, 76 g of the ethyl ester of monochloracetic acid and 22 g of sodium ethylate were used. The reaction was carried out in a solution of absolute ether. After the usual treatment in such cases the ether was distilled and the reddish liquid remaining was poured into a beaker. After standing

for some time the liquid crystallized out. After recrystallizing from alcohol slightly-yellow crystals with an m.p. of 125-126° were obtained. 35 g (45 %) was obtained.

Found %: N 6.10. $C_{16}H_{17}O_3N$. Calculated %: N 5.96.

The interaction of the ethyl ester of (p-dimethylaminophenyl)-pyroracemic acid with aniline. 5 g of the substance and 5 g of aniline were dissolved in 20 cc of ethyl alcohol and sealed in an ampoule. The ampoule was heated for 5 hours at 130-135°. After cooling, a yellow crystalline precipitate (5.8 g) was obtained and was then recrystallized from acetone. The m.p. was 157-158°. The same substance was obtained when the ampoule was heated at 200°.

Found %: N 10.04. $C_{17}H_{18}O_2N_2$. Calculated %: N 9.93.

SUMMARY

1. The reaction of the addition of ammonia and aniline with β-phenylglycidic acid was investigated. It was proved that under the influence of either of these reagents the oxide ring of glycidicacid is ruptured on the α-carbon side.

2. The reaction between ammonia and aniline and the ethyl esters of β-(p-methyl)- and β-(p-methoxyphenyl)-glycidic acids was investigated. It was found that the ethyl ester of β-(p-methylphenyl)-glycidic acid adds ammonia and aniline at the α-carbon atom. The ethyl ester of β-(p-methoxyphenyl)-glycidic acid adds aniline at the α-carbon atom but forms a tarry product with ammonia.

3. An attempt was made to synthesize the ethyl ester of (p-dimethylaminophenyl)-glycidic acid under the conditions of Darzens' reaction. It was shown that in this case isomerization of the glycidic ester into the ethyl ester of p-dimethylaminophenylpyroracemic acid takes place.

4. The infrared spectra of all the glycidic acids and their addition products investigated by us were determined. The characteristic absorption maxima of the oxide ring were determined.

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THE THERMAL DECOMPOSITION OF 2,3-BIS-(TRIMETHYLAMMONIUM)-BUTANE HYDROXIDE

Ya. M. Slobodin and O. Sergeev

In previous communications [1] it was shown that as a result of thermal decomposition ammonia bases containing two trimethylammonium groups in a chain of two or three carbon atoms are converted into the corresponding acetylenes. In the case of a three-carbon chain, allene is not formed whether the trimethylammonium groups are at adjacent carbon atoms or at the end of the chain. The thermal decomposition of trimethylammonium hydroxide [2] leads to the formation of practically pure divinyl. Neither methylallene, ethylacetylene nor dimethylacetylene were found among its decomposition products. This justifies the assumption that compounds containing two trimethylammonium groups in a chain of four carbon atoms would behave in a similar manner, being converted into divinyl and forming neither methylallene nor acetylenes. It must be pointed out, however, that in literature [3] there are indications that as a result of the thermal decomposition of the base obtained by the action of silver oxide on 2,3-bis-(trimethylammonium)-butane bromide not only divinyl but also methylallene and dimethylacetylene are formed. For the decomposition the authors used only 3.7 g of the ammonium salt (0.012 mole), which could be converted under optimum conditions into 0.1-0.15 liters of gas. The authors judged the composition of the gas by its reaction with maleic anhydride and with dilute sulfuric acid. In view of the discrepancy between these data and those indicated above we carried out an investigation of the thermal decomposition products of 2,3-bis-(trimethylammonium)-butane hydroxide. 12 g of 2,3-bis-(trimethylammonium)-butane bromide was used. The decomposition was carried out by distilling this salt with excess 40 % KOH solution. The decomposition products were collected in bromine cooled to 0°. As a result we obtained about 10 g of a crystalline bromide which after recrystallizing once from alcohol, melted at 116°. A mixed melt with divinyl tetrabromide showed no depression of the melting point (116°). Among the reaction products we found neither a high-melting bromide which would have corresponded to dimethylacetylene nor a liquid bromide corresponding to methylallene. It was, therefore, confirmed that neither acetylenes nor allenes are formed as a result of the thermal decomposition of bis-ammonium bases containing more than three carbon atoms in the chain.

As was noted in previous communications [1, 2, 4], unsaturated amines which readily reduce silver oxide, even in the cold, are formed together with hydrocarbons as a result of the thermal decomposition of bis-ammonium bases. To study the relationship of the unsaturated amines with silver oxide we used allylamine as a model in the present investigation. It was found that this amine is also readily oxidized by silver oxide. Acids were found in the reaction products. When heated on a boiling water bath the silver salts of the acids were partially decomposed with the formation of metallic silver (formic acid). The residue of the silver salts was recrystallized from water. The salt of propionic acid was obtained.

Found %: Ag 59.49. $C_3H_5O_2Ag$. Calculated %: Ag 59.67.

The formation of silver propionate could occur as a result of rearrangement of the allylamine into propylidenimine which is immediately saponified into propionaldehyde.

SUMMARY

1. It was shown that as a result of thermal decomposition 2,3-bis-(trimethylammonium)-butane hydroxide is converted into divinyl. Neither methylallene nor acetylenes were found in the reaction products.

2. Oxidation of allylamine by silver oxide leads to the formation of propionic acid.

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• Original Russian pagination. See C. B. Translation.

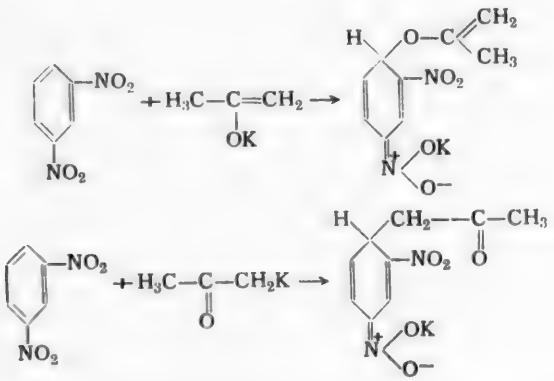
THE REACTIONS OF AROMATIC NITRO COMPOUNDS

1. THE INVESTIGATION OF THE JANOWSKY REACTION

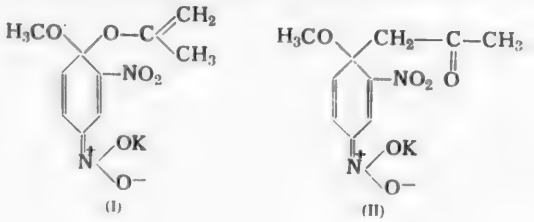
S. S. Gitis

As was established by Janowsky, the reaction between m-dinitrobenzene and acetone in the presence of alcoholic alkali produces a violet-red color [1]. The Janowsky reaction is also characteristic for other polynitro compounds [2] and for o- and p-nitrobenzene [3]. In spite of the widespread use of colored derivatives in analysis for the quantitative determination of aromatic hydrocarbons and their polynitro derivatives the mechanism of this interesting reaction has not been established. It was noted that the initially transparent solutions become turbid with time and turn brown. Until now it had not been possible to isolate the reaction products from the solution.

As was shown by our investigations, the reaction products can only be isolated from a medium of inert solvents – benzene, toluene, xylene and ether – in which the colored compounds are insoluble. If traces of moisture are present in the solvent the colored products become tarry. We assumed that the reaction of sodium-acetone or potassium-acetone with m-dinitrobenzene or other polynitro compounds is associated with the conversion of the benzoid form into the quinoid. Since potassium-acetone can be added in one of two forms the reaction could be of the following types:

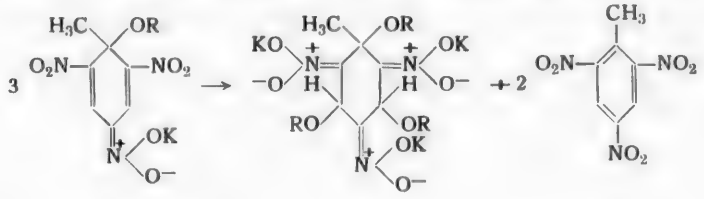


In order to resolve this problem the absorption spectra of colored solutions of 2,4-dinitroanisole with potassium-acetone and 2,4-dinitrophenyl-acetone with potassium methylate were determined. The formation of compounds (I) or (II) may be assumed, depending on whether the potassium-acetone is added in the keto- or the enol form. The formation of (II) is also possible for the product obtained by the addition of potassium methylate to 2,4-dinitrophenylacetone



The comparison of the absorption curves of the reaction product of 2,4-dinitrophenylacetone and potassium methylate and the addition product of potassium-acetone and dinitroanisole showed that these compounds are different. The first has λ_{max} 478 mμ and the latter 560 mμ. In consequence, the addition product has structure (I), i.e. the addition of potassium-acetone proceeds according to system A.

According to the analysis, when the synthesis is carried out it is only possible to isolate the di- and trisalt (the addition product of two or three molecules of sodium-acetone and one molecule of the dinitro- or trinitro derivative). The monosalt is evidently washed out during the process of separation, evidence of which is given by the color of the alcoholic and acetone washings. It must also be pointed out that the freshly-distilled amorphous product which is generally an intense red or violet-red color turns brown on standing even if kept in a hermatically sealed vessel. Disproportionation of the unstable monosalt into the disalt and trisalt evidently takes place.



R = residue of acetone in the enol form.

In contrast to the monosalt the di- and trisalts are insoluble in acetone but readily soluble in water. When the aqueous solutions of the di- and trisalts are boiled in the presence of an aqueous buffer solution of sodium acetate and acetic acid the intial polynitro compound is precipitated, which is an indication of the absence of polymerization.

EXPERIMENTAL

General method for obtaining addition products of sodium-acetone and polynitrocompounds. Synthesis of sodium-acetone. Sodium-acetone readily undergoes various changes in the presence of atmospheric oxygen and it was, therefore, prepared in a current of dry hydrogen. The synthesis was based on a method suggested by Freer [4]. A weighed amount of metallic sodium cut into fine strips was placed in a reaction flask. The sodium was covered with a layer of anhydrous o-xylene. After the air had been expelled for the system by hydrogen, acetone, diluted with o-xylene in the ratio of 1:75, was added from a dropping funnel. The reaction to produce the sodium-acetone lasted 24-26 hours. In the normal course of the reaction the solution remained transparent and only acquired a slight straw-yellow color. Sometimes the solution in the flask turned brown; when this occurred a red-brown precipitate which was evidently a mixture of the secondary reaction products of sodium and acetone (phorone, mesityle oxide) was deposited. The formation of the precipitate was assisted by the addition of acetone in excess of the theoretical quantity.

Synthesis of the addition products of sodium-acetone and polynitro derivatives. The solution of sodium-acetone in xylene was run into a thick-walled conical flask containing a solution of the dinitro compound in xylene. The first drops of sodium-acetone added to the solution of the polynitro compound produced a characteristic color (violet-red). Subsequent addition of sodium-acetone led to the formation of a dark-brown suspension. After standing for 12-14 hours the suspended substance settled out on the bottom of the flask in the form of an amorphous powder. The solution above the deposit turned a slightly yellowish color. The reaction was carried out at 16-18°. The amorphous powders obtained were washed with a mixture of acetone and xylene (1:1) until a sample gave a negative reaction for nitrol compounds with alkalized acetone, and were then washed several times with absolute ether. The products were dried in a vacuum desiccator over sulfuric acid for 2,3 hours and were kept in a well-paraffined vessel. Since it was intended to obtain the mono-and disalts (in the case of dinitro derivatives) and the trisalts (in the case of the trinitro compounds) the amounts of the initial products taken varied: 1/20 mole of polynitro compound, 1/20 mole of acetone and 1/40 g-at of sodium for the monosalt; 1/40 mole of polynitro compound, 1/10 mole of acetone and 1/20 g-at of sodium for the diaslt; 1/20 mole of polynitro compound, 1/10 mole of acetone and 1/40 g-at of sodium for the trisalt. The dried compounds were amorphous powders whose color varied from brown to brick-red. They rapidly darkened in air, being converted into tarry products.

As distinct from the derivatives of the dinitro compounds the addition products of sodium-acetone and tri-

nitro compounds were more stable. After standing for 5-10 minutes in air, however, a change in the color was noted and tarring occurred. When heated in an open flame they burnt with a flash and in a sealed tube they burnt with an explosion. It was readily soluble in water and in methyl alcohol, only slightly soluble in acetone and anhydrous alcohol and insoluble in benzene, toluene, xylene, ether, carbon tetrachloride and chloroform, etc.

The freshly-distilled addition product of sodium-acetone and m-dinitrobenzene colors an acetone solution, violet-red, an alcoholic solution is colored red-violet. The color of the solutions is indentical with that obtained by mixing a solution of m-dinitrobenzene in acetone with aqueous or alcoholic caustic potash; the temperature of decomposition is 55°.

Found %: C 42.80; H 5.00; N 8.62; Na 14.03. $C_{12}H_{14}O_6N_2Na_2$. Calculated %: C 43.90; H 4.26; N 8.53; Na 14.02.

The addition products of sodium-acetone and polynitro compounds obtained are given in Table 1.

Name of the polynitro compound	Color of the products isolated	Temperature of decomposition	Found (%)		Empirical formulae of the compound	Calculated (%)		Note*
			N	Na		N	Na	
o-Dinitrobenzene	Yellow-brown	—	8.53	16.54	$C_{12}H_{14}O_6N_2Na_2$	8.53	14.02	Calculated for the disalt
p-Dinitrobenzene	Greenish-brown	—	8.78	14.52	$C_{12}H_{14}O_6N_2Na_2$	8.53	14.02	
2,4,6-Trinitrotoluene	Brick-red	55-60°	9.52	15.30	$C_{16}H_{20}O_9N_3Na_3$	9.00	14.77	Calculated for the trisalt
3,6-Dinitro--o-xylene	Light-brown	48	7.89	12.71	$C_{14}H_{16}O_6N_2Na_2$	7.90	13.10	Calculated for the disalt
2,6-Dinitro--p-xylene	Yellow	49-50	8.15	13.00	$C_{14}H_{16}O_6N_2Na_2$	7.90	13.10	
2,4,6-Trinitro--m-xylene	Brown-red	68-70	7.99	15.00	$C_{17}H_{22}O_9N_3Na_3$	8.73	14.34	Calculated for the trisalt

* Analyses of the carbon and hydrogen contents of these compounds were not carried out because of explosions in the combustion tube. Intense shocks did not make it possible to collect the CO_2 and H_2O quantitatively.

SUMMARY

1. A system was proposed for the reaction of polynitro compounds with acetone in the presence of alkali (Janowsky's reation).

2. Under the conditions in which addition products of sodium-acetone and polynitro derivatives are obtained the latter add the maxium number of molecules of sodium-acetone, equal to the number of nitro groups taken for the reaction of the polynitro compound.

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THE REACTIONS OF AROMATIC NITRO COMPOUNDS

II. THE REACTION OF TRINITROANISOLE AND TRINITROPHENETOLE WITH ALCOHOLATES

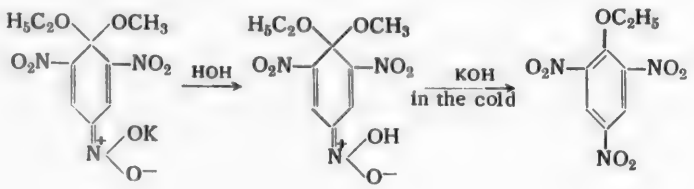
S. S. Gitis and A. I. Glaz

In spite of the considerable number of works devoted to the explanation of the structure of colored products formed by the interaction of aromatic trinitro derivatives with alcoholates their properties have not been closely studied. The reaction products can by no means always be isolated from the solution although, in general, the solutions have an intense-red color.

The esters of picric acid, for example, trinitroanisole and trinitrophenetole readily form colored products with potassium alcoholates. Comparing the various points of view regarding the structure of these colored compounds[1], preference must be given to the mechanism suggested by Meisenheimer [2], according to which the metal of the alcoholate is added to the oxygen of the nitro group and the alkoxy group to the carbon of the benzene ring. If this system is correct the addition products of potassium ethylate with trinitroanisole and potassium methylate with trinitrophenetole must be identical. To verify this assumption we synthesized both products and compared their properties. It was found that the addition product of potassium ethylate and trinitroanisole and of potassium methylate and trinitrophenetole crystallize differently. The first occurs in the form of tabular orange crystals while the second is obtained as large purple-red needles. At low temperature, high dilutions and after long standing larger and brighter crystals of the trinitroanisole derivative with a color closer to that of the trinitrophenetole derivative are formed. Larger and brighter crystals are also formed when the colored product is obtained by the action of an aqueous solution of caustic potash (40 %) on an alcoholic solution of trinitroanisole.

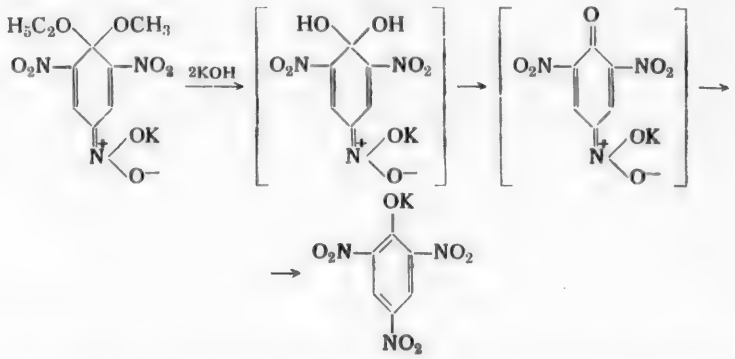
Despite the apparent difference in the crystals of both products they were identical, a fact which was established by comparing their absorption spectra in a solution of acetone (λ_{max} of the trinitroanisole derivative 485 mμ, and the same value for the trinitrophenetole derivative). In addition, the electrical conductivity of an acetone solution of the colored salt was measured. The equivalent electrical conductivity of a 0.008 N solution was 75. If we compare this value with the λ of organic salts it approximately corresponds to sodium acetate. This justifies the conclusion that compounds of this type are dissociated.

In order to establish the structure of the addition products of potassium ethylate and trinitroanisole Meisenheimer decomposed them by means of sulfuric acid. He obtained a mixture of trinitroanisole and trinitro phenetole [2]. We noted that, on standing, aqueous solutions regenerate trinitrophenol without an admixture of trinitroanisole. When decomposed by water the addition product of N-C_3H_7OK and trinitrophenetole gives the propyl ester of picric acid. By this means N-butyl and isoamyl esters of picric acid were isolated. The hydrolysis evidently proceeds according to system 1.



At the same time as this conversion takes place, potassium picrate is obtained, according to system 2, particularly when heated and if a sufficient amount of water is used.

System 2



The formation, primarily of esters of picric acid with a more complex hydrocarbon radical, as a result of hydrolysis, is unusual. It is well known that the alcoholysis of compounds with mobile haloid takes place more easily with sodium methylate, the next in order of promotion of the reaction being the ethylate, etc. We consider that a possible explanation of an unusual reaction of this type is the different acidity of simple and more complex alcohols. In actual fact, with system 1, during hydrolysis there is always a certain amount of caustic potash in the reaction mixture. Subsequently, the caustic potash, by acting on the unchanged addition product, forms an alcoholate primarily with the more acid alkoxy group. This mechanism is further confirmed by the fact that during hydrolysis of the addition product of ethyl cellosolve and trinitroanisole, trinitroanisole is formed, i.e. in this case the more acid residue of the ethyl ester of ethylene glycol is removed from the addition product. If the aqueous solutions are heated hydrolysis according to system 1 is accelerated and the amount of alkali is considerably increased; this facilitates the splitting off of two alkoxy groups with the formation of potassium picrate, according to system 2.

It is an interesting fact that as a result of the action of a buffer solution (an aqueous 0.1 N solution of sodium acetate and acetic acid) on the addition product of trinitroanisole and potassium ethylate a mixture of trinitroanisole and trinitrophenetole is obtained, i.e. in this instance because of the presence of free caustic potash the reactions cannot proceed according to systems 1 and 2; this is confirmed by our proposed mechanism for the reaction.

In conclusion we would like to point out that since the reactions of higher alcoholates with trinitroanisole and trinitrophenetole followed by hydrolysis give good yields these reactions could serve as a convenient method for preparing the higher esters of picric acid.

EXPERIMENTAL

General method of obtaining the addition products of potassium alcoholates and esters of picric acid. 0.01 mole of the trinitro ester was dissolved in 25-100 cc of alcohol (depending on the solubility) with heating. 0.01 mole of caustic potash dissolved in 10-15 cc of the alcohol containing the alkoxy group to be introduced was added dropwise to the cooled solution with stirring. An intensive blood-red coloration was observed immediately and after several minutes (but in some cases, immediately) crystals of various red shades (depending on the alcoholate used) with a specific metallic luster were precipitated. When heated, all the colored products decomposed with an explosion without having melted. They were completely insoluble in ether, benzene, xylene, chloroform and carbon tetrachloride.

The addition product of C_2H_5OK and trinitroanisole. Orange-red tablets with a decomposition temperature of 200°. Yield 90%.

Found %: K 12.13, 11.81. $C_9H_{10}O_8N_3K$. Calculated %: K 11.93

The addition product of N-C_3H_7OK and trinitrophenetole. Red-brown hexagonal prisms with a decomposition temperature of 210°. Yield 58%.

Found %: K 10.84. $C_{11}H_{14}O_8N_3K$. Calculated %: K 10.98.

The addition product of N-C_4H_9OK and trinitroanisole. Brown-red needles and prisms with a decomposition temperature of 215-217°. Yield 89%.

Found %: K 10.77. $C_{11}H_{14}O_8N_3K$. Calculated %: K 10.98.

The addition product of iso-C_4H_9OK and trinitroanisole. Orange-red tetragonal plates with a decomposition temperature of 220°. Yield 93 %.

Found %: K 10.81. $C_{11}H_{14}O_8N_3K$. Calculated %: K 10.98.

The addition product of iso-$C_5H_{11}OK$ and trinitroanisole. Red-orange prisms with a decomposition temperature of 261-262°. Yield 59 %.

Found %: K 11.00 $C_{12}H_{16}O_8N_3K$. Calculated %: K 10.56.

The addition of esters of picric acid. 1 g of the orange product, dried in air, was dissolved in 100-150 cc of water. To obtain the isoamyl ester it was necessary to double the amount of water used. After standing for a day a yellow deposit of the ester of picric acid with an alkoxy residue of the less-acid alcohol was deposited. The esters of picric acid were obtained pure; the melting points of the latter coincided with the data in the literature without recrystallization (Table 1).

TABLE 1

Name of the ester of picric acid	Melting point	Yield (%)
Ethyl (trinitrophenetole)	78-79°	75
N-Propyl	43-44	61
N-Butyl	35-36	74
Isobutyl	52.5-53.5	46
Isoamyl*	44-45	77

SUMMARY

1. It was shown that the addition products of potassium alcoholates and trintroanisole or trinitrophenetole can be converted into the higher esters of picric acid.

2. A mechanism for the conversion of the addition products of alcoholates into the esters of picric acid and picrates was proposed.

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Dnepropetrovsk State University

* According to the data in literature the m.p. is 56°. The author does not indicate which isoamyl ester was used.
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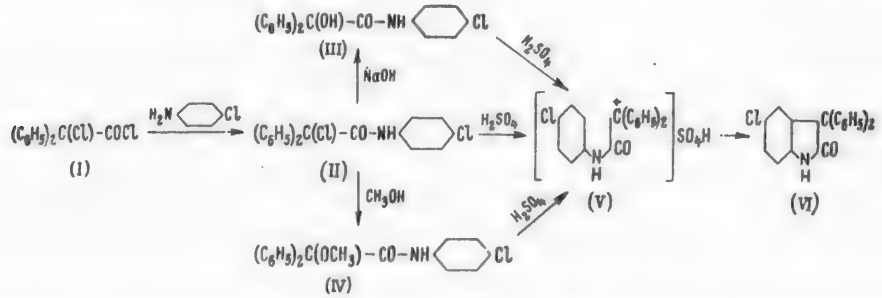
STUDIES IN THE FIELD OF HETEROCYCLIC CHEMISTRY

XXXI. SYNTHESIS OF 3,3-DIARYLOXINDOLS AND 1-METHYL-3-OXO-4,4--DIPHENYLTETRAHYDROISOQUINOLINE BASED ON ARYLAMIDES OF DIPHENYLCHLORACETIC AND DIPHENYLALKOXYACETIC ACIDS

P. A. Petyunin, I. S. Berdinsky and N. G. Panferova

We have shown that arylamides of diarylglycolic acids under the action of mineral acids are very easily and almost quantitatively converted into 3,3-diaryloxindole derivatives [1]. This method was subsequently used for synthesizing 6-, 7-, and 8-membered heterocyclic systems [2, 3], and also extended to arylamides of diphenylchloroacetic acid [4]. But the latter, owing to limited availability, was used in only two cases.

At the present time, in view of disclosures in the literature of available methods of obtaining the acid chloride of diphenylchloroacetic acid [5], it becomes possible to widen the field of use of arylamides of diphenylchloroacetic acid, and also to include in our studies the arylamides of diphenylalkoxyacetic acids. The present communication is devoted to the accomplishment of this task. Using the p-chloroanilide of the acids named, we may represent the proposed synthesis as follows:



Synthesis of the arylamides of diphenylchloroacetic acid (Table 1) is effected by reaction of the acid chloride of diphenylchloroacetic acid (I) with aromatic amines in a dry ether medium. Very active chlorine is contained therein.

Thus, for example, in heating p-chloroanilide of diphenylchloroacetic acid (II) with aqueous-dioxan—alkali solution, the p-chloroanilide of benzilic acid (III) is formed with good yield; and, on heating with methyl alcohol, we obtain the p-chloroanilide of diphenylmethoxyacetic acid (IV). Table 2 gives the properties of the arylamides of diphenylmethoxyacetic acid that we obtained.

It is known that the arylamides of diarylglycolic acids, in relation to mineral acids, exhibit basic properties [1]. These properties are especially emphasized with the introduction of electron-donor substitutes into the phenyl radicals by means of carbinolic carbon [4].

In the arylamides of diarylglycolic acids (VII, X=OH) π-electrons of the benzene rings are linked with $\backslash C-O-$ and $\backslash C-\backslash C-$ bonds. Basic properties depend on linkage with the help of the $\backslash C-O-$ bond.

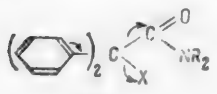
TABLE 1

Structure of R in $(C_6H_5)_2CClCONHR$	Yield (in %)	M.p.	Nitrogen content (in %)	
			Found	Calculated
o-$CH_3C_6H_4$ . . .	92.9	82—83°; benzine prisms	3.96, 4.07	4.16
p-BrC_6H_4	83.7	127—128; benzine needles	3.33, 3.35	3.35
α-$C_{10}H_7$	89.7	130—131; benzine needles	3.68, 3.53	3.76
$C_6H_5CH(CH_3)$	92.9	79—80; benzine prisms	4.10, 4.20	4.04

TABLE 2

Structure of radicals in $(C_6H_5)_2C(OCH_3)CONRR^1$		Yield (in %)	M.p.	Nitrogen content (in %)	
R	R^1			Found	Calculated
o-$CH_3C_6H_4$ . . .	H	75.8	105—106°; benzene prisms	4.17, 4.27	4.23
p-BrC_6H_4	H	90	174—175; toluene needles	3.47, 3.45	3.53
α-$C_{10}H_7$	H	85.7	133—135; methanol flakes	3.63, 3.92	3.81
C_6H_5	C_2H_5	90	158—159; methanol flakes	4.20, 4.10	4.05

As experiments have shown, the compounds obtained by us (VII, X = Cl, O = Alk) have a basic character indicating the presence in their molecules of linkages through the $>C=X$ bond, and also the possible closing of the heterocyclic systems therein. As a matter of fact by action on (II) and (IV) of concentrated sulfuric acid, they, as also (III), undergo acidolysis, with formation of a reddish brown color, corresponding to the structure of a halochromic salt (V). On standing for a short time the color disappears, and after diluting these solutions with water 5-chlor-3,3-diphenyloxindol (VI) separates out with almost quantitative yield.



(VII)

In Table 3 are given experimental results in the synthesis of derivatives of 3,3-diaryloxindol and 1-methyl--3-oxo-4,4-diphenyltetrahydroisoquinoline (IX) from arylamides of diphenylchloroacetic acid (Method A) and diphenylalkoxyacetic acid (Method B).

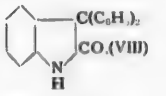
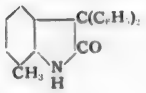
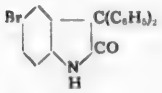
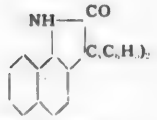
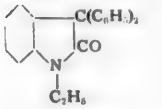
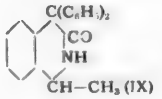
EXPERIMENTAL

p-Chloroanilide of diphenylchloroacetic acid (II). A solution of 5.3 g* of (I) was poured with stirring into a cooled solution of 5.1 g p-chloroanilin in 20 ml ether. The separating deposit of the p-chloroanilin hydrochloride was filtered off and washed with dry ether. The reaction product was separated from the ether solution after removing the solvent. Yield was 5 g (70.4%). It is soluble in benzene, ether, benzine, and acetic acid. With concentrated sulfuric acid it gives a disappearing brown color, accompanied by separation of hydrogen chloride. It crystallizes from benzine in the form of needles, agglomerating into druses or nodules, with m.p. of 124-125°.

Found %: N 3.97, 4.03. $C_{20}H_{15}ONCl_2$. Calculated %: N 3.76

*The acid chloride of diphenylchloroacetic acid, with a yield of 85.5 % and b.p. of 150-154° (4 mm) was obtained as per literature data [5].

TABLE 3

Formula	Method A		Method B		Literature data
	Yield (in %)	M. p.	Yield (in %)	M.p.	
 (VIII)	—	—	93—95	225°	225° [6]
	95	254—255°	97	254—255	254—255 [7]
	94.5	284	97.8	284	284 [1]
	94.4	254	96.7	254	254 [1]
	—	—	95.6	159—160	158—159 [6]
 (IX)	94.5	272	—	—	272 [2]

Note — 3,3-diphenyloxindol (VIII) was obtained from anilides of diphenylmethoxy- and diphenylethoxyacetic acids. Synthesis of the latter was effected according to Klinger [8].

p-Chloroanilide of benzilic acid (III). 1.2 g (II) was dissolved with heating in 10 ml dioxan to which had previously been added 1 ml of a 10 % caustic soda solution. On cooling the solution was poured into 50 ml water. The precipitate was filtered off and crystallized from glacial acetic acid. The yield was 1 g (87.7 %). With concentrated sulfuric acid a disappearing reddish brown color formed; needles with m.p. of 210-212°.

Found %: N 3.99, 4.24. $C_{20}H_{16}O_2NCl$. Calculated %: N 4.14.

p-Chloroanilide of diphenylmethoxyacetic acid (IV). 1 g (II) was dissolved with heating in 10 ml methanol. On cooling the reaction product separated in an analytically pure form. Yield was 0.9 g (90 %). It is soluble in alcohol, acetic acid, and benzene. With concentrated sulfuric acid it gives a disappearing reddish brown color. It crystallizes with mother of pearl luster (from methanol) with m.p. 182-183°.

Found %: N 4.06, 3.84. $C_{21}H_{18}O_2NCl$. Calculated %: N 3.98.

5-Chlor-3,3-diphenyloxindol (VI). Method A. Concentrated sulfuric acid was added in small amounts with stirring to a solution of 1.2 g (II) in 10 ml of galcial acetic acid, until the disappearing reddish brown coloring ceases; whereupon abundant separation of hydrogen chloride and foaming of the reaction mass could be observed. After pouring into 50 ml cold water the separated precipitate was treated in the usual way. Yield 1.04 g (96.1 %).

Method B. 1 g (IV) was dissolved in 10 ml glacial acetic acid and then 7 ml concentrated sulfuric acid was added. After cessation of the reddish brown coloring the reaction product was separated, as in the preceding test. Yield 0.84 g (94.4 %).

Method C. 10 ml of concentrated sulfuric acid was added to a solution of 1 g (III) in 10 ml galcial acetic acid. On completion of the reaction (disappearance of the reddish brown coloring), the product was poured into 50 ml water, and treated as described above. Yield 0.8 g (85.1 %). It is difficultly soluble in alcohol, benzene, and toluene; easily soluble in glacial acetic acid; forming needles from glacial acetic solution, with m.p. 263--265°.

Found %: N 4.17, 4.25. $C_{20}H_{14}ONCl$. Calculated %: N 4.38.

SUMMARY

1. By reacting the acid chloride of diphenylchloroacetic acid with aromatic amines a series of arylamides of diphenylchloroacetic acid, not described in the literature, were obtained, and their properties studied.

2. It was shown that the chlorine in these arylamides of diphenylchloroacetic acid is very active (mobile) and easily replaces the hydroxyl through action of alkali or the alkoxyl by action of alcohols.

3. A series of arylamides of diphenylalkoxyacetic acids not described in the literature was obtained,and their properties studied.

4. It was shown that the arylamides of diphenylalkoxyacetic acids. as also those of diphenylchloroacetic and benzilic acids, under the action of concentrated sulfuric acid, undergo acidolysis with formation of the halochromic salt.

5. The method was extended to obtain 3,3-diaryloxindols and 4,4-diphenyl-1-methyl-3-oxotetrahydroisoquinoline from arylamides of diphenylchloroacetic acid.

6. For the first time arylamides of diphenylalkoxyacetic acids were used for the synthesis of 3,3-diphenyloxindols.

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STUDIES IN ORGANIC INSECTOFUNGICIDES

XXVI. NEW METHOD OF SYNTHESIZING MIXED ESTERS OF DITHIOPHOSPHORIC ACIDS

N. N. Melnikov, A. F. Grapov and K. D. Shvetsova-Shilovskaya

Recently in our laboratory a new method of synthesizing mixed esters of dithiophosphoric acid by combining acid esters of dithiophosphoric acid with unsaturated compounds was developed [1-3]. Some of the esters of dithiophosphoric acid synthesized in this way appeared to be interesting insecticides, justifying further study [4, 5]. More recently this reaction was used also for the synthesis of various other esters of dithiophosphoric acid [6, 7]. In developing our researches for studying the relation between the insecticidal properties of organic phosphorus compounds and their structure, and in the search for new insecticides, we undertook the synthesis of mixed esters of dithiophosphoric acid, having the general formula (I).

$(RO)_2$ PSSAr (I) $(RO)_2$PSOAr (II)

The synthesis of this type of dithiophosphoric acid esters was of great interest in view of the fact that many of the mixed esters of thiophosphoric acid of general formula (II) are very active insecticides of the contact kind. More especially O,O-diethyl-O,4-nitrophenylthiophosphate (Thiophos) and O,O-dimethyl-O,4-nitrophenylthiophosphate (Metaphos) are very active insecticides and are widely used in agriculture.

The synthesis of mixed esters of dithiophosphoric acid similar to Thiophos and Metaphos was also of interest owing to the possibly higher photochemical stability of these compounds and their intestinal effect. In the patent literature there are references to the contact insecticial effect present in several of the simplest mixed esters of dithiophosphoric acid [8].

In order to obtain mixed esters of dithiophosphoric acid of the general formula (I) only one method is described in the literature: reaction of dialkylchlorothiophosphates with thiophenols in the presence of bases [8]. But this method has several disadvantages that hinder its use in the production of mixed esters of dithiophosphoric acid containing different functional groups in the aromatic radical. In order to obtain mixed esters of dithiophosphoric acid we used the reaction of acid esters of dithiophosphoric acid with aromatic diazo compounds, which may be represented in the following general scheme.

$$(RO)_2PSSK + ArN_2X \rightarrow (RO)_2PSSAr + N_2 + KX$$

The reaction proceeds at a relatively low temperature, and the mixed dithiophosphoric acid esters form with fully satisfactory yields. We used metallic copper as catalyst. In order to obtain good yields of the mixed esters of dithiophosphoric acid from the aryldiazonium salts and acid esters of dithiophosphoric acid, the reaction solution must not contain nitric acid or nitrogen oxides, as these latter oxidize the acid esters of dithiophosphoric acid into the corresponding disulfides, and a greatly contaminated product is obtained.

$$2(RO)_2PSSH + [O] \rightarrow (RO)_2PSSSSP(OR)_2 + H_2O$$

The reaction of formation of mixed esters of dithiophosphoric acid from aryldiazonium salts and dialkyl-dithiophosphates apparently proceeds as a homolytic mechanism, as is the case with most other processes of this type.

No.	Compound	B.p. (pressure in mm)	Yield (in %)	d_4^{20}	n_D^{20}	Empirical formula	MR_D Found	MR_D Calc	P (in %) Found	P (in %) Calc	Conc. of preparation giving a 50% kill of rice weevils (Calandra oryzae) in 50 hours
1	$(CH_3O)_2PSSC_6H_5$	95—97°(0.1)	54	1.2466	1.5927	$C_8H_{11}O_2S_2P$	62.20	62.38	13.42, 13.23	13.22	0.021 ± 0.003
2	$(C_2H_5O)_2PSSC_6H_5$	102.5—104.5(0.1)	48	1.1823	1.5629	$C_{10}H_{15}O_2S_2P$	72.02	71.63	11.8, 11.8	11.81	0.03 ± 0.003
3	$(CH_3O)_2PSSC_6H_4CH_3$ (2)	101—102.5(0.1)	46.5	1.1644	1.5660	$C_9H_{13}O_2S_2P$	—	67.00	11.8, 11.6	11.99	—
4	$(CH_3O)_2PSSC_6H_4CH_3$ (3)	102.5—102.8(0.1)	40	1.1729	1.5662	$C_9H_{13}O_2S_2P$	—	67.00	11.82, 11.65	11.99	—
5	$(CH_3O)_2PSSC_6H_4CH_3$ (4)	104.5—105(0.15)	27.5	1.2136	1.5829	$C_9H_{13}O_2S_2P$	66.73	67.00	12.08, 11.80	11.99	0.03 ± 0.003
6	$(C_2H_5O)_2PSSC_6H_4CH_3$ (2)	118—118.5(0.2)	47.5	1.1696	1.5642	$C_{11}H_{17}O_2S_2P$	76.83	76.25	11.42, 11.23	11.24	0.07 ± 0.007
7	$(C_2H_5O)_2PSSC_6H_4CH_3$ (3)	105—107(0.09)	42	1.1781	1.5624	$C_{11}H_{17}O_2S_2P$	76.11	76.25	11.13, 11.08	11.24	0.042 ± 0.0045
8	$(C_2H_5O)_2PSSC_6H_4CH_3$ (4)	110—112(0.12)	51	1.1779	1.5639	$C_{11}H_{17}O_2S_2P$	76.32	76.25	11.35, 11.45	11.24	0.035 ± 0.0045
9	$(C_2H_5O)_2PSSC_6H_4Cl$ (3)	104.5—106.5(0.08)	45	1.2538	1.5730	$C_{10}H_{14}O_2ClS_2P$	77.99	76.97	10.53, 10.42	10.44	—
10	$(C_2H_5O)_2PSSC_6H_4Cl$ (4)	122—123(0.2)	51.3	1.2627	1.5750	$C_{10}H_{14}O_2ClS_2P$	77.67	76.79	10.32, 10.6	10.44	—
11	$(C_2H_5O)_2PSSC_6H_4NO_2$ (4) *	137—139(0.1)	41.6	—	—	$C_{10}H_{14}O_4NS_2P$			10.1, 10.0	10.08	0.004

The method proposed by us for obtaining mixed esters of dithiophosphoric acid is, to a certain extent, analogous to the reaction of formation of xanthogenic acid esters described by Leucart [9], and to the reaction for obtaining aromatic esters of dithiocarbamic acid developed by Clifford and Lichty [10].

The mixed dithiophosphoric acid esters synthesized by us and their properties are given in the Table. Tests of the insecticidal properties of the synthesized compounds, made by P. V. Popov, showed that all the compounds, in respect to contact insecticidal activity, are somewhat inferior to Thiophos, but O,O-diethyl-S,4-nitrophenyldithiophosphate proved to be the most active among them.

EXPERIMENTAL

All the mixed dithiophosphoric acid esters were obtained under the following typical conditions, with small deviations for individual compounds: an aqueous solution of an equimolecular amount of the dithiophosphoric acid ester and catalyst (0.1 g copper per 0.1 mole of reacting mixtures) was added to an aqueous solution of the diazonium salt (after preliminary oxidation of excess nitric acid by passing air through the solution). The reactants were mixed 0-2° and the reacting mixture then heated over a water-bath to 40-50°. Heating at this temperature was continued until separation of gaseous nitrogen ceased. After this, the mixture was cooled down to 10-15° and the ester extracted, the solution being dried, and after distilling off the ester the reaction product was fractionated in vacuum. Redistillation in vacuum was repeated at least twice. The compounds obtained are listed in the table. The yields given are for 2- or 3-time distilled product.

SUMMARY

1. A new method was developed for obtaining mixed dithiophosphoiic acid esters by reacting dithiophosphoric acid esters with aryldiazonium salts. It was shown that, by the new method, mixed esters of dithiophosphoric acid, containing various functional groups in the aromatic radical, may be obtained in good yield. The contact insecticidal activity of the compounds obtained is lower than that of the corresponding esters of thiophosphoric acid.

2. It was suggested that formation of the mixed esters of dithiophosphoric acid proceeds as a homolytic mechanism.

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STUDIES IN ORGANIC INSECTOFUNGICIDES

XXVII. NEW METHOD OF OBTAINING CHLOROTHIOPHOSPHORIC ACID ESTERS

N. N. Melnikov, Ya. A Mandelbaum, E. Sventsitsky and Z. M. Bakanova

Among the insecticides and acaricides of contact and systemic action, the mixed esters of thiophosphoric acid, formed by reacting various hydroxylic compounds with dialkylchlorothiophosphates in the presence of bases, have obtained the widest use in agriculture. Also compounds such as Thiophos, Metaphos, Mercaptophos, Metsistox, O-methyl-O-ethyl-O,4-nitrophenylthiophsophate, and several others obtained from dialkylchlorothiophosphates, have attained great importance in the fight against plant pests. In relation thereto we have undertaken a systematic study of different methods of producing these interesting compounds.

One of the interesting methods of obtaining dialkylchlorothiophosphates is that of reacting phosphorus thiotrichloride or alkyldichlorothiophosphates with various metal alcoholates. But the use of alkaline metal alcoholates does not ensure constant stable yields [1], and as a result of inconsiderable changes in reaction conditions there is an appreciable reduction in yield of the dialkylchlorothiophsophate; nor does the use of aluminum alcoholates in this reaction give sufficiently good yields [2], as may be well understood, because in reacting phosphorus thiotrichloride with an aluminum alcoholate, there are a large number of secondary reactions.

With a view to discovering suitable methods of producing dialkylchlorothiophosphates, it was of interest to study the reaction of phosphorus and alkyldichlorothiophosphates with magnesium alcoholates, and in the first place with magnesium ethylate [3]. From the experiments carried out it was possible to establish that the reaction of magnesium ethylate with phosphorus thiotrichloride proceeds in the following manner:

$$2PSCl_3 + (C_2H_5O)_2Mg \longrightarrow 2(C_2H_5O)PSCl_2 + MgCl_2 \quad (1)$$

$$2(C_2H_5O)PSCl_2 + (C_2H_5O)_2Mg \longrightarrow 2(C_2H_5O)_2PSCl + MgCl_2 \quad (2)$$

$$2(C_2H_5O)_2PSCl + (C_2H_5O)_2Mg \longrightarrow 2(C_2H_5O)_3PS + MgCl_2 \quad (3)$$

Reaction No. 1 proceeds most quickly and No. 3 most slowly; this is quite understandable because the first chlorine atom in phosphorus thiotrichloride is replaced by the alkoxyl even in reacting with alcohol [4]. The varying rate of reaction of phosphorus thiotrichloride, alkyldichlorothiophosphate, and dialkylchlorothiophsophates, with magnesium ethylate permits the production of dialkylchlorothiophosphate with good yields exceeding 70 %. Small amounts of trialkylthiophsophates, formed in accord with Reaction No. 3, are obtained as secondary products.

The quality of the magnesium ethylate used has an appreciable effect on the yield and composition of the resulting dialkylchlorothiophosphate. It was found from special experiments that the best yields are obtained from the use of a magnesium ethylate containing two molecules of alcohol. On removal of alcohol from the magnesium ethylate,an inactive substance of gray color is formed, from the use of which a low yield of dialkylchlorothiophosphate is obtained. The chlorothiophosphoric esters obtained by us, together with their properties, are given in the Table.

EXPERIMENTAL

1. Preparation of magnesium ethylate: Metallic magnesium, in the form of chips or powder, is placed in a flask with reflux condenser and calcium chloride tube, and enough anhydrous alcohol is poured in to completely

cover the magnesium. A small crystal of iodine is also added together with 3 to 5 drops of carbon tetrachloride. After the reaction has become sufficiently vigorous, as evidenced by hydrogen separation, the remaining quantity of anhydrous alcohol is poured in. The amount of alcohol chosen is 2-1/2 to 3 times in excess of that required by the reaction equation. After vigorous formation of hydrogen has stopped, the reaction mixture is boiled with reflux condensing until all the magnesium has been dissolved (1.5 to 2 hours). This magnesium ethylate solution is used for production of chlorothiophosphoric acid esters.

Compound	B. p. pressure (mm)	Yield (%)	d_4^{20}	n_D^{20}	Empirical formula	P content (%)	
						Found	Calc.
$(C_2H_5O)_2P(=S)-Cl$ . . .	96—98° (25)	77	—	—	$C_4H_{10}O_2ClSP$	—	—
$CH_3O, C_2H_5O)P(=S)-Cl$ . . .	79—80 (17)	75.5	1.2506	1.4740	$C_3H_8O_2ClSP$	—	—
$C_2H_5O, iso\text{-}C_3H_7O)P(=S)-Cl$.	84—85 (10)	70	1.1561	1.4620	$C_5H_{12}O_2ClSP$	15.2, 15.01	15.35
$C_2H_5O, C_4H_9O)P(=S)-Cl$ . . .	126—127 (22)	70	1.1432	1.4660	$C_6H_{14}O_2ClSP$	14.37, 14.41	14.30
$C_2H_5O, iso\text{-}C_5H_{11}O)P(=S)-Cl$.	131—132 (20)	70	1.0885	1.4620	$C_7H_{16}O_2ClSP$	13.32, 13.11	13.50

2. Reaction of phosphorus thiotrichloride with magnesium ethylate. 34 g (0.2 mole) of phosphorus thiotrichloride is placed in a flask with reflux condenser, thermometer, and mechanical stirrer rotating at not less than 150 rpm, and magnesium ethylate (prepared from 5.3 g metallic magnesium) is gradually added with stirring. The magnesium ethylate is added at such a rate that the temperature of the reaction mixture is within 30 to 45°. Addition of the ethylate requires about 45 min. After all the magnesium ethylate has been added, the temperature of the reaction mass is maintained at 45° with vigorous stirring for 2 hrs. The mixture is then diluted with cold water acidified with a small amount of hydrochloric acid, the oil separated, washed with water, dried, and fractionated in vacuum. The fraction 96-98° (25 mm) is collected n_D^{25} 1.4676, d_4^0 1.2017. Yield 77 %.

3. Reaction of ethyldichlorothiophosphate with magnesium ethylate. Under the above-described conditions 15.4 g (82 %) of diethylchlorothiophosphate was obtained from 17.8 g ethyldichlorothiophosphate and magnesium ethylate (prepared from 1.4 g metallic magnesium and 40 ml anhydrous alcohol). Addition time of magnesium ethylate was 20 min , temperature 25-30°; holding time, 1 hr at 35-45°. Under similar conditions all the other dialkylchlorothiophates listed in the Table were synthesized.

SUMMARY

A new method was developed for obtaining dialkylchlorothiophosphates by reacting magnesium ethylate with alkyldichlorothiophosphates or with phosphorus thiotrichloride. Yields of dialkylchlorothiophosphates by this method range from 70 to 90 %.

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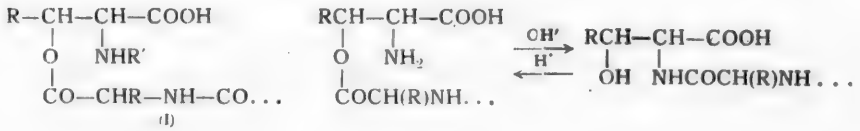
STUDY OF THE PROPERTIES OF O-PEPTIDES OF β-HYDROXYAMINO ACIDS

AMMONOLYSIS AND AMINOLYSIS REACTIONS

M. M. Botvinik, S. M. Avaeva, M. I. Konovalova and V. I. Ostoslavskaya

O-Peptides of β-hydroxyamino acids, type (I) have lately received much attention. This has been due in the first place to the separation of a new antibiotic – asaserine [1], and, in the second place, to the constantly growing interest in the behavior of different functional groups in albumens and peptides and their significance in metabolic processes. In earlier published researches [2] the synthesis of a large number of N-benzoyl-O-peptides of serine and threonine was described, and experiments for study of the specific properties of the O-peptide (ester) bond were begun. Thus, the ability of proteolytic ferments to split this bond was demonstrated [3]. This fact was a new actual confirmation of the hypothesis of ester bonds in albumens. Recently such grouping was discovered in procollagen [4]. Similar grouping is suggested in actinomycin [5].

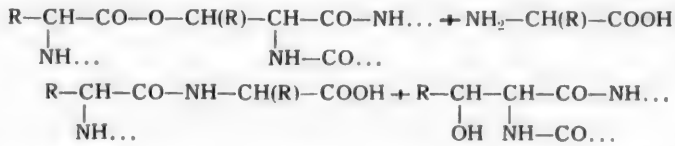
The second special feature of O-peptides of β-hydroxyamino acids is the ease with which they isomerize into N-peptides [6].



(I)

R = radical, H; R' = H, acyl

The O-peptides of β-hydroxyamino acids may be regarded as special esters of which the alcoholic radical contains the amino group; and their isomerization into N-peptides is an intramolecular aminolysis proceeding spontaneously. Such ease of reaction indicates high mobility of the O-peptide bond, and permits the suggestion that aminolysis may take place also intermolecularly. In such case, in reacting O-peptides of β-hydroxyamino acids with amino acids, new peptides will be formed and the O-peptides will appear as carriers of amino acid groups or radicals.



Brenner [7] emphasizes the importance of amino acid esters in the process of biological synthesis of peptides and describes the fermentative synthesis of the peptides of methionine and threonine from their ethyl esters. We have discovered the ability of the O-peptides of β-hydroxyamino acids to react with glycocoll ethyl ester under the action of chymotrypsin, with formation of the corresponding glycocoll peptides. Recently Schwyzer [12] has shown amino acid esters may be activated by the introduction of electrophilic groups, e.g. cyanomethylic. By the production of the cyanomethyl esters of amino acids he developed a simple method of synthesizing peptides.

In the present work the first experiments in the ammonolysis and aminolysis of esters of O-peptides of serine

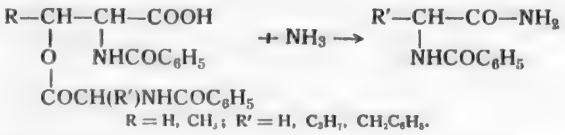
and threonine, formed through the hydroxyl group of hydroxyamino acids are given. The experiments were undertaken with N-benzoyl-O-benzoylphenylalanyl-, N-benzoyl-O-benzoylvalyl- and N-benzoyl-O-hippuryl serines, N-benzoyl-O-benzoylphenylalanyl threonine and N-benzoyl-O-benzoylphenylalanyl ethanolamine. The necessary O-peptides were synthesized by an earlier-developed method [2]. O-Hippuryl-N-benzoyl and O-benzoylvalyl-N-benzoyl serines were first obtained. During the synthesis of the O-peptides it was found that their yields largely depended on reaction temperature conditions (Table 1).

TABLE 1

Name of O-peptide	Test temperature	Yield %
O-Benzoylphenylalanyl-N-benzoylserine	50—70°	58
	20	22
O-Benzoylvalyl-N-benzoylserine	100	20
	50—60	55
O-Benzoylglycyl-N-benzoylserine	50—60	0
	30—40	0
	20	82

Such dependence of yield of O-peptides of N-benzoyl serine on temperature conditions is evidently due to the varying stability of oxazolone hydrochlorides.

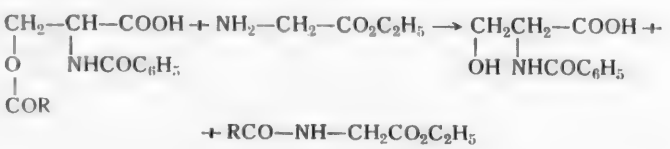
The O-peptides obtained were treated with ammonia, and it was found that they reacted very easily, forming the corresponding amides of benzoylphenylalanine, benzoylvaline and hippuric acid.



$R = H, CH_3$; $R' = H, C_2H_7, CH_2C_6H_5$.

The reaction proceeds at room temperature. Yields of amides vary from 15 to 100% according to the peptide and ammonia concentration. Thus, with O-benzoylphenylalanyl-N-benzoyl and O-benzoylvalyl-N-benzoyl serines, amide yields fell with decreasing ammonia condensation (Table 2). An experiment was undertaken with the ethyl ester of benzoylphenylalanine, and it was shown that with 25 % ammonia the reaction proceeds slowly and incompletely. This once again confirms the special behavior of the ester bond in the O-peptides of β-hydroxyamino acids.

Experiments were then made in reacting O-peptides of N-benzoyl serine with glycocoll ethyl ester. The results are given in Table 3.



COR = benzoylphenylalanyl, benzoylvalyl, hippuryl.

The first experiments, undertaken with benzoylphenylalanyl-N-benzoyl serine and glycocoll ethyl ester at room temperature, showed that the aminolysis reaction does not take place so easily — under these conditions it did not proceed at all. The conditions of aminolysis were studied with O-hippuryl-N-benzoyl serine by way of example. The tests were made in ethyl acetate solution at room temperature, with heating also in the presence of triethylamine. In all cases the reaction was limited by the formation of the salt of N-acyl-O-peptide and of glycocoll ethyl ester that are precipitated. Since it is soluble in dilute acetone further experiments were made in this solvent, when marked resinification was observed, and the dipeptide ester did not separate. Only by heating the O-peptide and glycocoll ethyl ester in a flask for 16 hrs at 60-70° did the benzoylpeptide ester separate.

TABLE 2

Ammonolysis of N-benzoyl-O-peptides of Serine, Threonine, and Ethanolamine

Peptide	Ammonia %	Time hrs	Yield of amide %	M.p.	Remarks
O-Benzoylphenylalanyl-N-benzoylserine	25	4	100	194—196°[8]	Rapid precipitation in alcoholic solution
	25	1	86		—
	12.5	1	86		—
	6	1	70		—
	3	1	43		—
	1.5	1	26		—
O-Benzoylvalyl-N-benzoylserine	25	5	60	217—218	Rapid precipitation in alcoholic solution
	12	7	40		—
	12	5	60		—
	6	2.5	25		—
	6	5	40		—
	3	24	15		—
	3	2	13		—
O-Hippuryl-N-benzoylserine	25	1	70	181—185[9]	No precipitate; hippuryl amide is separated after partial conc. of solution
	12.5	2	66		
	6	2.5	63		
	3	2	68		
O-Benzoylphenylalanyl-N-benzoylthreonine	12.5	2	52	194	Rapid precipitation
Amide O-benzoylphenylalanyl-N-benzoylserine	12	15	41	194	In alcoholic solution
O-Benzoylphenylalanyl-N-benzoylethanolamine	12	15	53	196	Rapid precipitation in alcoholic solution
Ethyl ester of benzoylphenylalanine	25	2	25	—	—

Yields of this latter did not exceed 30%, and, as follows from the data in Table 3, it depends on the reagents ratio. Thus the possibility was shown in principle of aminolysis of the ester bond in the O-peptides of benzoyl serine. Experiments undertaken under the same conditions with glycol ethyl ester and the ethyl esters of benzoylphenylalanine and hippuric acid respectively showed that, with these esters, there is practically no reaction. This once again confirms the highly labile state of the ester bond in the O-peptides of benzoyl serine.

EXPERIMENTAL

1. Synthesis of O-benzoylvalyl-N-benzoyl serine.* 2-Phenyl-4-isopropyloxazolone hydrochloride prepared from 4.8 g of benzoylvaline was added to a solution of 4.7 g benzoyl serine in 40 ml anhydrous dioxan and stirred to complete dissolution. The mixture was left overnight and then heated for 8 hours at 50-55°. The needlelike precipitate was filtered off by suction. The yield of the first part of O-benzoylvalyl-N-benzoyl serine was 3 g. The mother liquor was dried in vacuum and the residual oil was crystallized by addition of aqueous acetone. The crystalline second part thus obtained was washed with benzene and water. The yield was 2.33 g. Total yield of crude product was 55%. After recrystallizing from aqueous alcohol the m.p. was 184-185°. It was soluble in acetone and hot alcohol, but not soluble in water, dichloroethane and carbon tetrachloride. The compound has not been described in the literature.

Found %: C 64.2, 64.04; H 5.99, 5.86; N 6.79, 6.72. $C_{22}H_{24}O_6N_2$. Calculated %: C 64.08; H 5.82; N 6.79.

2. Synthesis of O-hippuryl-N-benzoyl serine. 2-Phenyloxazolone hydrochloride obtained from 5 g hippuric acid was added to a solution of 3.75 g benzoyl serine in 40 ml anhydrous dioxan. A precipitate at once began to form. The reaction mixture was stirred for 10-12 hours. The precipitate was separated and a further 0.95 g of

*Undertaken by O. M. Shibanova.

TABLE 3

Aminoysis of the Ester Bond in the O-peptides of Benzoyl Serine with Glycocoll Ethyl Ester

No. of Exp.	Name of peptide	Reagent ratio	Temperature	Time hrs	Solvent	Catalyst	Compound obtained	Yield (in %)	M.P.
1	O-Hippuryl-N-benzoylserine	1 : 8	24°	10	Absolute ethyl acetate	—	Peptide salt and glycocoll A*	92	145°
2	do	1 : 8	70—77	6—7	do	—	do	92	145
3	„	1 : 8	70—77	6—7	„	triethylamine	do	—	145
4	„	1 : 8	24	10	Acetone, aq (70%)	—	do	—	—
5	„	1 : 8	60—70	16	—	—	B** of benzoylglycyl glycine	10	116 [10]
6	„	1 : 27	60—70	16	—	—	do	29	—
7	O-Benzoylphenylalanyl-N--benzoylserine	1 : 27 1 : 8	60—70 60—70	16 16	—	—	B of benzoylphenylalanyl glycine	31	156 [11]
8	O-benzoylvalyl-N-benzoyl-serine	1 : 27	60—70	16	—	—	B of benzoylvalyl glycine	24	159—160
9	B of benzoylphenylalanine	1 : 27	60—70	16	—	—	B of benzoylphenylalanine	97	89—90 [8]
10	Ethyl hippurate	1 : 27	60—70	16	—	—	Ethyl hippurate	—	55—56

* A is ester

** B is ethyl ester

peptide separated from the mother liquor after evaporating off the solvent under vacuum. The total yield of crude product was 82.3 %. It was recrystallized from aqueous acetone and then from aqueous alcohol, m.p. was 161-161.5°. The substance has not been described in the literature.

Found %: C 61.09, 61.17; H 4.95, 5.01. $C_{19}H_{18}O_6N_2$. Calculated %: C 61.59; H 4.86.

3. Ammonolysis of O-peptides of N-benzoyl serine, benzoyl threonine, and benzoyl ethanolamine. 0.2 g of each of the peptides listed in Table 2 were treated with 5 ml ammonia solution; whereby rapid solution of the substance was observed. Within a short time the solution set in a solid mass. The amide was filtered off, washed with water, and recrystallized from aqueous alcohol. Experimental results are given in Table 2.

4. Reaction of benzoylphenylalanine ethyl ester with ammonia. 5 ml of 25 % aqueous ammonia was added to a solution of 0.2 g of the ethyl ester of benzoylphenylalanine. On standing 0.05 g of the original ester was precipitated (m.p. 94°). Within an hour the reaction mixture was diluted with twice its volume of water, whereby a further 0.1 g of the initial ester separated out. After subsequent dilution of the mother liquor with water the benzoylphenylalanine amide was precipitated. Yield 0.03 g.

5. Aminolysis of the O-peptides of N-benzoyl serine with glycocoll ethyl ester (ethylamino acetate); (a) Weighed portions of the O-peptides of N-benzoyl serine and glycocoll ethyl ester were heated in a sealed tube for 16 hours at 60-70°. The reaction mass was treated with chloroform, the insoluble precipitate filtered off, washed with chloroform solution of 1 N hydrochloric acid, soda solution, and with water. It was then evaporated in vacuum and the residual oil treated with ether. It crystallizes on standing. The separated crystals of the benzoylpeptide ester were recrystallized in aqueous alcohol. The experimental results are given in Table 3.

(b) 0.5 g of glycocoll ethyl ester was added to a solution of 0.2 g of N-benzoyl-O-hippuryl serine in 17 ml absolute ethyl acetate. Within 10 min a copious deposit of precipitate began. The reaction mixture was stirred at room temperature for 30 hrs. The precipitate was separated and washed with ethyl acetate. It is soluble in water, dilute acetone, aqueous alcohol and dilute ethyl acetate. The substance gives a ninhydrin reaction. When treated with hydrochloric acid the initial O-hippuryl-N-benzoyl serine separates. Thus, the compound obtained is the salt of glycocoll ethyl ester and O-hippuryl-N-benzoyl serine m.p. 145°.

(c) 0.2 g O-hippuryl-N-benzoyl serine and 0.5 g glycocoll ethyl ester were heated in ethyl acetate solution for 7 hrs at 70-75° with stirring. A copious precipitate soon formed, giving the ninhydrin reaction, yield 0.24 g, m.p. 140°. The compound is the salt of glycocoll ethyl ester and O-hippuryl-N-benzoyl serine.

(d) 0.2 g O-hippuryl-N-benzoyl serine, 0.5 g glycocoll ethyl ester, and 0.06 g triethylamine were heated in ethyl acetate solution for 6 hrs at 70-75°, with stirring. The precipitate was treated with aqueous alcohol. On standing the salt of glycocoll ethyl ester and O-hippuryl-N-benzoyl serine separated out from the solution, m.p. 145°. Mixing a sample of the melt with the earlier obtained products showed no depression.

6. Reaction of the ethyl esters of benzoylphenylalanine and of glycocoll. 0.204 g of benzoylphenylalanine ethyl ester and 2 g of that of glycocoll were heated in an ampoule for 16 hrs at 60-70°. The reaction mixture was treated in the same way as in the experiments with the O-peptides. After evaporating the chloroform solution the benzoylphenylalanine ethyl ester separated to the amount of 0.198 g.

7. Reaction of ethyl hippurate with glycocoll ethyl ester. 0.19 g of ethyl hippurate and 2 g of glycocoll ethyl ester were treated in the same way as in the experiments with O-peptides. Ethyl hippurate separated out from the chloroform solution.

8. Synthesis of benzoylvaline amide. 5 ml of 25 % aqueous ammonia was added to 0.394 g of 2-phenyl--4-isopropyl-5-oxazolone hydrochloride. After rapid solution precipitate began to form. The benzoylvaline amide was recrystallized from aqueous alcohol, m.p. 218°.

Found %: C 65.24, 65.18; H 7.26, 7.24; N 12.70 $C_{12}H_{16}O_2N_2$. Calculated %: C 65.46; H 7.27; N 12.73.

9. Synthesis of benzoylvalylglycine ethyl ester. 5 g of glycocoll ethyl ester was added to 4 g of 2-phenyl--4-isopropyl-5-oxazolone hydrochloride. With strong heating the oxazolone dissolved, and within a few minutes a precipitate began to form. Chloroform was added to the reaction mixture which was then left standing for a time. The chloroform solution was then separated, the chloroform driven off, and the residue recrystallized from aqueous acetone, m.p. 161-162°.

Found %: N 8.37, 9.40. $C_{16}H_{22}O_4N_2$. Calculated %: N 9.15.

SUMMARY

The ammonolysis and aminolysis reactions of O-peptides of N-benzoyl-β-hydroxyamino acids have been studied. It was found that the O-peptide (ester) bond reacts easily with ammonia and glycocoll ethyl ester, and has much greater lability than the ester bond in benzoylamino acid ethyl ester.

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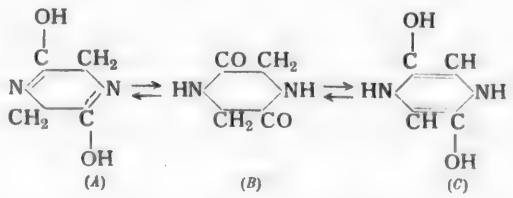
ON MODELS OF ALBUMIN MICROSTRUCTURE

II. PRODUCTION OF N-AMINOACYLDIKETOPIPERAZINES FROM THE IMINOESTER (O,O-DIBENZYL-2,5-DIHYDROPYRAZINE)

L. N. Akimove and Z. V. Kiryukhina *

Of the four possible forms of bonding diketopiperazines with amino acids only two – production through the enol form of diketopiperazines – have hitherto been experimentally achieved. The only work in this connection that should be considered is the attempt to synthesize the O,O-dibenzyl ester of glycine anhydride [1]. It was obtained from the silver salt of diketopiperazine, and was the only well-substantiated [2] production through the enol form of diketopiperazine. Tautomeric conversions are possible for these diketopiperzines, associated with migration of the hydrogen atoms to oxygen from nitrogen atoms of the imino groups or from the carbon atoms of the methylene groups of the ring.



Only form (B) is known in a free state. The silver salt may be regarded as a derivative of form (A) of the diketopiperazine; although the possibility of its existence in another form under certain conditions is not excluded.

It was earlier established [3] that, in reacting O,O-dibenzyl-2,5-dihydropyrazine with amines, amidines of the dihydropyrazine series are formed in quantitative yield. In this way dipicrates and dihydrochlorides of diphenyl- and dipropyl-2,5-anhydropyrazines were obtained.

The reaction of O,O-dibenzyl-2,5-dihydropyrazine with glycocoll and tyrosine esters leads evidently to formation of linear polypeptide amidines [4]. This possibility of using O,O-dibenzyl-2,5-dihydropyrazine for the synthesis of amidines was extended by us, and the use of this ester has been shown in the present work in synthesizing aminoacyl derivatives of diketopiperazine. As a result, the N,N'-diphthalylalanyl- and N,N'-diphthalylleucyl-diketopiperazines were obtained. This confirmed the earlier suggestion on the possibility of O,O-dibenzyl-2,5--dihydropyrazine yielding derivatives not only by way of oxygen but also of nitrogen [5].

Proceeding from the reaction proposed by Karrer for synthesizing O,O-dibenzyl-2,5-dihydropyrazine from the silver salt of diketopiperazine and benzyl chloride, we studied the reaction of this slat of diketopiperazine with compounds containing active chlorine. It was necessary to study this reaction with derivatives of chlorocarbonic acid. For this purpose the ethyl and benzyl esters of this acid were prepared. We supposed that the reaction of the silver salt of diketopiperazine with the chlorocarbonic ester should lead (from analogy with O,O-dibenzyl--2,5-dihydropyrazine) to the compound (I). A compound of this structure is a mixed anhydride of the enol form of diketopiperazine, and the chlorocarbonic ester, and in reacting with amino acids would lead to the formation of an amidine.

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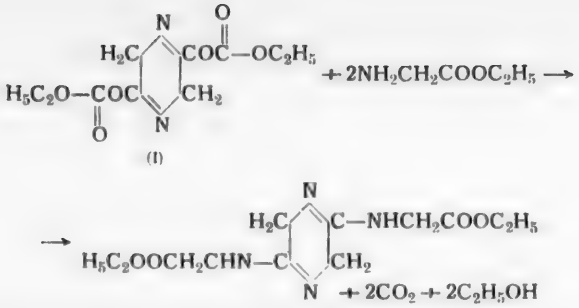
* Deceased.



Formation of an amidine linkage in this reaction would be analogous with that of the peptide bond in the mixed anhydride method.

But many repetitions of the above-described reaction with modifications did not lead to the desired result. Negative results were obtained when the chlorocarbonic ester was replaced by carbobenzoxy chloride also. But the reaction of the silver salt of diketopiperazine with acetylchloride led to formation of N,N'-diacetyldiketopiperazine. In this case the acetyl derivative was obtained through the nitrogen of the diketopiperazine, in good agreement with the production therefrom of aminoacyl derivatives.

Thus, the behavior of the silver salt of diketopiperazine behaves analogously in reaction both with carbonyl chloride and with the (acid) chlorides of amino acids, but differs from the reaction with esters (ethyl and benzyl) of chlorocarbonic acid.

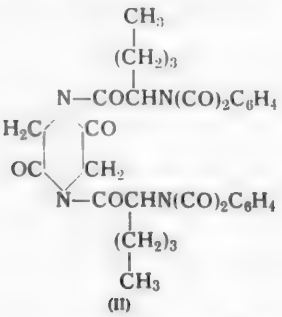
EXPERIMENTAL

1. Phthalylleucine was synthesized by the method developed for inactive isoleucine [6]. The phthalyl derivative of norleucine was thus obtained. M. p. 105-107°. In the literature the m.p. is 107.5°. Yield was 76%.

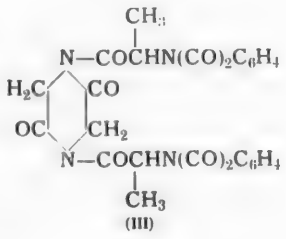
2. Phthalylleucyl chloride. Unlike the method referred to [6] the reaction was effected in an anhydrous benzene medium according to the directions indicated for phthalylleucyl chloride [7]. M.p. 59-60°. Yield 83%.

3. N,N'-diphthalylleucyl-(glycine) anhydride (II). 1.1 g of O,O-dibenzyl-2,5-dihydropyrazine [1] was heated with 2.1 g of phthalylleucine chloride in 30 ml of anhydrous xylene for 3 hrs. On completion of the reaction the xylene filtrate was concentrated to an oily residue. After addition of ether and prolonged standing, crystallization began. M. p. 193°. Yield 46%. Insoluble in organic solvents.

Found %: C 64.20; H 5.36; N 9.60. $C_{32}H_{32}O_8N_4$. Calculated %: C 63.99; H 5.37; N 9.33.



(II)



(III)

In order to confirm the structure the following experiments were undertaken:

a) Establishing the amino acid constitution: 0.1 g of the substance was hydrolyzed with 10 % HCl for 32 hrs. The hydrolyzate, after removing the hydrochloric acid, was chromatographed on paper. Solvent: water, acetic acid.

b) Reaction with hydrazine: 0.5 g N,N'-diphthalylleucyl-(glycine) anyhdride and 1.6 ml of 1 M alcoholic solution of hydrazine hydrate were heated in 6 ml anhydrous alcohol for 1 hr. The solution was cooled to room

temperature, the precipitate filtered off, washed with alcohol, and recrystallized at 50° from hot alcohol. Part of the residue remaining from the alcohol treatment, from its m.p. of 316° and properties, is diketopiperazine; weight 0.1 g. The phthalylleucyl hydrazine was separated from the alcoholic filtrate and hydrolyzed with 10 % hydrochloric acid. The paper chromatogram revealed only leucine.

Found %: N 17.21. $C_{11}H_{17}O_3N_3$. Calculated %: N 17.56.

c) The copper biuret complex test: A solution of 4 % NaOh and 4 % $CuCl_2$ solution was added to N,N'-diphthalylleucyl-(glycine) anhydride until a nonvanishing precipitate of $Cu(OH)_2$ formed. After standing for 24 hrs the solution was filtered and spectraphotometrically examined. Maximum absorption was found in wavelength of 570 mμ.

4. Phthalylalanine. 10 g alanine was mixed with 16.6 g phthalic anhydride. The mixture was melted at 160-170° over an oil bath. Water was added to the hot melt. Crystallization followed on cooling. The substance was recrystallized from water. M. p. 163.5°. According to the literature the m.p. is 164°. Yield 22.5 g (92 %).

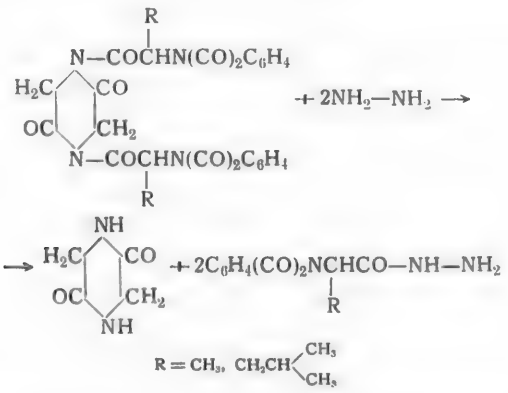
5. Phthalylalanyl chloride. 9 g phthalylalanine and 8.5 g PCl_5 were heated at 60° in 110 ml anhydrous benzene until solution of the deposit (first 25 min) on stirring. The reaction mixture was heated for another hour at 60°. On completion the benzene was distilled in vacuum. The residue was dissolved in a small amount of benzene and precipitated with isopentane. The chloride precipitate was filtered off. M. p. 73°. According to the literature the m.p. is 73° [9]. Yield 8.2 g (85 %).

6. N,N'-diphthalylalanyl-(glycine) anhydride (III). O,O-dibenzyl-2,5-dihydropyrazine [1] and 2 g (2 M) of phthalylalanyl chloride were heated in ten times the amount of anhydrous xylene for 4 hrs. On heating it all dissolved. The precipitate forming on cooling was filtered off. The xylene filtrate was concentrated in vacuum. The remaining oil was crystallized with addition of acetone. The residue was filtered off and washed with acetone. After recrystallizing from nitrobenzene the m.p. was 285°; yield 44 %. The substance is not soluble in organic solvents.

Found %: C 60.55; H 3.97; N 10.75. $C_{26}H_{20}O_8N_4$. Calculated %: C 60.48; H 3.90; N 10.85.

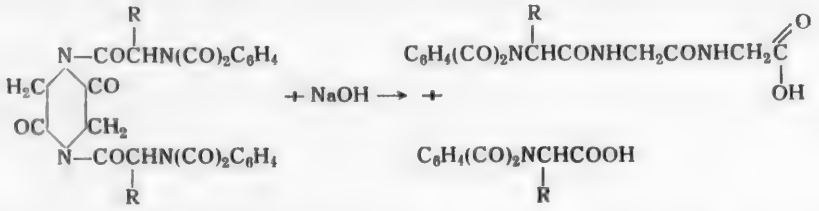
Confirmatory evidence of structure was based on paper chromatographic results (appearance in the acid hydrolyzate of alanine and glycocoll), test of reaction products with hydrazine (diketopiperazine and phthalylalanyl hydrazide), and study of the copper biuret complex (maximum absorption 570 mμ for the melt products).

Reaction of the synthesized compounds with hydrazine is of interest. Unlike the removal of the phthalyl block that was earlier noted by us [10], decomposition of N,N'-diphthalylleucyl-(glycine) anhydride and of N,N'-diphthalylalanyl-(glycine) anhydride proceeds with the aid of hydrazine, as first observed by us with derivatives of phenylalanine anhydride of an aminoacyl character [11]. This decomposition leads to quantitative separation of the glycine anhydride and formation of the hydrazides of the corresponding phthalylamino acids according to the scheme:



The biuret reaction, negative for all the N,N'-diamino-acyldiketopiperazines, takes place on long standing of these latter with 4 % alkali. Breakdown of the copper biuretic complexes by hydrochloric acid, and separation

thereby of phthalylleucylglycyl glycine [in the case of N,N'-diphthalylleucyl-(glycine) anhydride], and of phthalylalanylglycyl glycine [in the case of N,N'-diphthalylalanyl-(glycine) anhydride] confirm the structure of the compounds synthesized by us. and prove their decomposition according to the following scheme:



7. Reactions of the silver salt of glycine anhydride. a) With chlorocarbonic esters: 5 g of the silver salt of glycine anhydride [1] is mixed with 3 ml of chlorocarbonic ester in anhydrous dioxan in a chlorinator (with stirrer) for 3-5 days. On completion of the reaction the precipitate was filtered off and washed with dioxan. It weighed 4.9 g. From its properties it appeared to be the original substance. A residue was separated from the dioxan filtrate (by condensation thereof and precipitation with acetone) which proved to be diketopiperazine.

b) With carbobenzoxy chloride: 3 g of the silver salt of glycine anhydride and 5.5 g of carbobenzoxy chloride were stirred with anhydrous dioxan for 3 days. As a result, the unchanged silver salt of diketopiperazine separated.

c) With acetyl chloride: 4 ml of acetyl chloride was added to 2 g of the silver salt of glycine anhydride in 10 ml benzene with cooling. As a result N,N'-diacetylglycine anhydride was separated from the reaction. After recrystallizing from alcohol the m.p. was 102°, which accords with the literature [12].

SUMMARY

1. The N-aminoacyl derivatives of glycine anhydrides have been obtained: N,N'-diphthalylleucyl-(glycine) anhydride and N,N'-diphthalylalanyl-(glycine) anhydride.

2. Their decomposition under the action of hydrazine into glycine anhydride and the hydrazides of the corresponding phthalylamino acids was confirmed.

3. The absence of activity of the diketopiperazine silver salt in reactions with the chlorocarbonic ester and carbobenzoxy chlorides was noted.

4. Reaction of the diketopiperazine silver salt with acetyl chloride leads to formation of the N,N'-diacetyldiketopiperazine.

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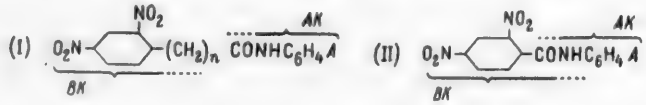
• Original Russian pagination. See C. B. Translation.

ON COLOR PHENOMENA WITH THE ARYLAMIDES OF O,O-DIBENZYL--2,4-DINITROBENZOIC ACID

REFLECTION AND ABSORPTION SPECTRA

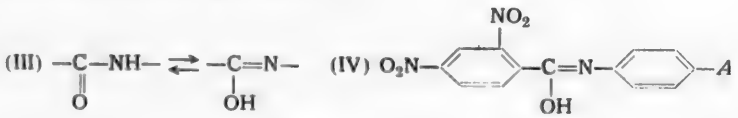
E. A. Smirnov

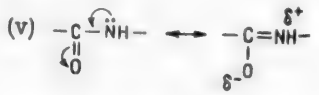
We have previously discussed the color phenomena with arylamides of 2,4-dinitrophenylacetic, 2,4-dinitrohydrocinnamic [1] and γ-(2,4-dinitrophenyl) butyric [2] acids of the general formula (I), where A is one of the electron-donor groups OCH_3, OH, $N(CH_3)_2$ disposed in the meta- or para- position in respect to NH, and n = 1, 2, 3.



The presence of a sufficiently deep visible color even with derivatives of dinitrophenylbutyric acid (n = 3) – where the possibility of interaction of an electron-acceptor system BK with an electron-donor system AK within the molecule, along the chain, is completely excluded owing to the presence in the chain of three CH_2-groups – led us to the conclusion that a decisive role in the color phenomena of the compounds mentioned is played by direct reaction of electron-acceptor and electron-donor systems with the aid of "exomolecular forces" [3], i.e. those forces which govern the formation of complex combinations between nitrocompounds and aromatic amines, phenols, and hydrocarbons. The similarity of the light absorption curves with analogous representatives of all three series of compounds, and likewise also in the case of absorption curves constructed on the basis of total absorption of individual components of which one contains the electron-acceptor and the other the electron-donor system, is good confirmation of the conclusion stated.

In the present communication the analogous derivatives of 2,4-dinitrobenzoic acid (II) are dealt with, in which the CONH groups is the bonding as for the benzene rings. This group, as is known, is capable of tautomerization (III), and therefore, in the given case, the possibility is not excluded of the formation of a complex conjugated chain of double bonds (IV). The latter may be formed also as a result merely of displacing the electron couple of a nitrogen atom without shifting the proton (V)



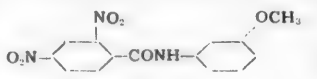
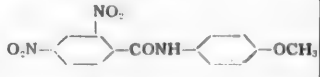
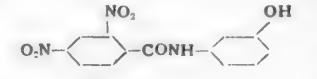
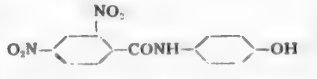
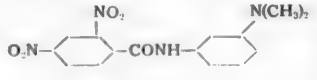
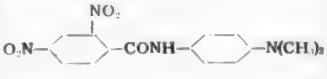


Visual observation and reflection spectra. In Table 1 a list of the compounds we have synthesized together with their indicated colors both in crystalline and in powder form is given.

As may be seen from Table 1, all the compounds listed have a visible color, varying from pale yellow with

compounds containing the weakest electron-donor group m-OCH_3 (No. 1), to deep red, nearly balck, with compounds having the strongest electron-donor group p-$N(CH_3)_2$ (No. 6)

TABLE 1

No.	Formula of Compound	Color of substance	
		in crystals	in powder
1		Pale yellow	Nearly colorless
2		Brownish yellow	Orange-yellow
3		Yellow	Yellow
4		Yellow	Yellow
5		Dark red*	Brownish red
6		Dark red, nearly black	Reddish brown

* The second form of this compound is orange-red in the crystalline form and reddish orange in the powder form.

Comparison of the colors of these compounds with the colors of the corresponding derivatives of 2,4-dinitrophenylacetic acid (Table 2, Nos. 2 and 3) shows that, as a rule, the first are colored somewhat more deeply than the second, although the difference in color is generally small. This may be seen also in the light reflection curves (Fig. 1-3) which, in most cases with analogous compounds of both series, are disposed close to each other and often intersect. Only with compounds having the strongest electron-donor group $N(CH_3)_2$ is a stronger bathochromic bend in the curve observed, at the transition from dinitrophenylactic acid derivatives to the corresponding derivatives of dinitrobenzoic acid (Fig. 1 and 3, Curves 3 and 4). In the case of compounds with the p-OH and with m-OCH_3 group, the reflection curves of the dinitrobenzoic acid derivatives are disposed even somewhat more hypsochromically in comparison with those of the corresponding dinitrophenylacetic acid derivatives, that respond to the higher coloring of the first as compared with the coloring of the second (Fig. 1 and 2, Curves 1 and 2). In Table 2, also, are given the colors of the analogous mononitro- derivatives both of benzoic and of phenylacetic acids. This permits an understanding of the extent to which introduction of the second group NO_2 affects the coloring in both cases. Our previous communications [1, 2] showed that the introduction of the second NO_2 group into the molecule of the arylamides of p-nitrophenylacetic, p-nitorhydrocinnamic, and γ-(p-nitrophenyl)-butyric acids, in all cases leads to a considerable deepening of the color of the resulting compounds. It was to be expected that, also in the given case, introduction of the second nitro group would be associated, too, with a deepening of color of the corresponding arylamides. From the data of Table 2 and reflection Curves (Fig. 4-6) it can be seen , as a matter of fact, that most of the dinitrobenzoyl derivatives are colored more deeply than the corresponding mononitrobenzoyl derivatives, where the greatest bathochromic effect, due to introduction of the second NO_2 group, is observed with the presence in the compound of the p-$N(CH_3)_2$ group (Fig. 4, Curves 3 and 4). A sufficiently marked bathochromic bending of the reflection curve is noted also with compounds having the p-OCH_3, m-OH, and m-$N(CH_3)_2$ groups. But with the presence in the compound of the p-OH or m-OCH_3 group, introduction of the second NO_2 group produces – as is by no means strange – a small hypsochromic effect (Fig. 4 and 5, Curves 1 and 2); as a result of which the dinitro derivatives obtained also show, as was mentioned above, a lighter coloring than the

TABLE 2

No.	Types of compounds	Substituting electron-donor groups (A) and color of corresponding compounds (in powder)					
		m-OCH_3	p-OCH_3	m-OH	p-OH	m-$N(CH_3)_2$*	p-$N(CH_3)_2$
1	4-$O_2NC_6H_4CONHC_6H_4A$	very light yellow	light yellow	light yellow	orange-yellow	yellowish brown	light red
2	2,4-$(O_2N)_2C_6H_3CONHC_6H_4A$	nearly colorless	orange-yellow	yellow	yellow	brownish red*	reddish brown
3	2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4A$	nearly colorless	yellow	light yellow	bright yellow	brownish yellow	brownish red
4	4-$O_2NC_6H_4CH_2CONHC_6H_4A$	colorless	colorless	pale yellow	nearly colorless	orange-yellow	yellowish orange

* The second form – reddish-orange color (as powder)

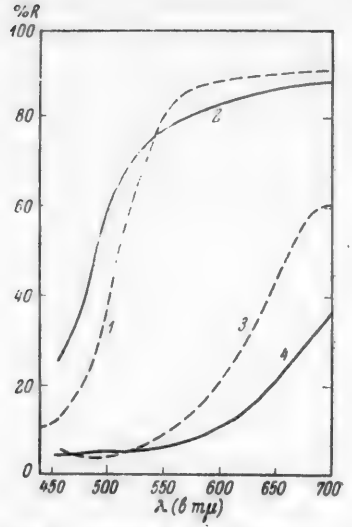


Fig. 1. Curves of light reflextion.
1) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4OH$-p,
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-p,
3) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4N(CH_3)_2$-p,
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-p.

corresponding dinitrophenylacetic acid derivatives. From the data of the same Table 2 it is evident that, with phenylacetyl derivatives, introduction of the second nitro group in all cases produces a bathochromic effect.

Light absorption spectra. The absorption curves of dinitrobenzoyl derivatives containing the supplementary electron-donor group (A) in the para- position are shown in Figs 7 and 8a (Curves 1). Both these curves have in each case well-marked absorption bands: one, shortwaved, shown in the ultraviolet part of the spectrum, with λ_{max} 278 mμ for the compound with the p-$N(CH_3)_2$ group and λ_{max} 249 mμ for the compound with the p-OH group; while the other is longwaved, appearing in the visible part of the spectrum. This band has a clearly expressed maximum only for the compound with the p-$N(CH_3)_2$ group (λ_{max} 408 mμ; for the compound with the p-OH group its position can be only approximately determined (about 324 mμ).

In Figs 8, b and 9 (Curves 1) are shown the absorption curves of the analogous compounds containing the supplementary electron-donor group in the meta-position. These curves have the same absorption bands as the corresponding curves of the para- isomers, displaced somewhat toward the shorter waves. The long-wave band of the compound containing the $N(CH_3)_2$ group is considerably narrower and less marked than the corresponding band for the para- isomer. It has no clearly expressed

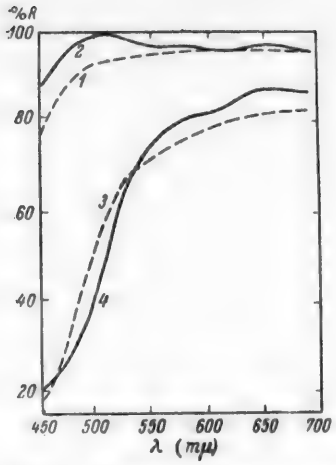


Fig. 2. Curves of light reflection.

1) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4OCH_3$-m,
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OCH_3$-m,
3) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4OCH_3$-p,
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OCH_3$-p.

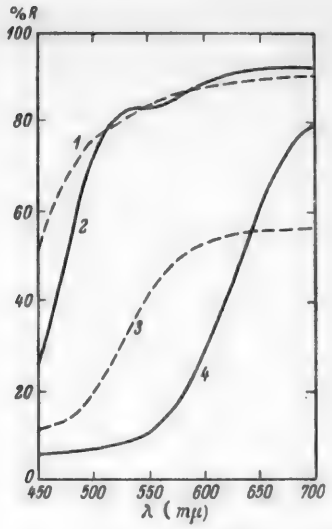


Fig. 3. Curves of light reflection.

1) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4OH$-m,
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-m,
3) 2,4-$(O_2N)_2C_6H_3CH_2CONHC_6H_4N(CH_3)_2$-m,
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-m.

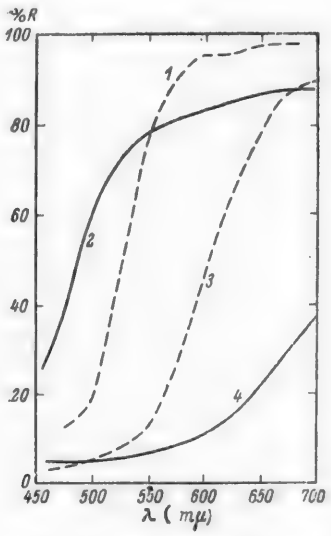


Fig. 4. Curves of light reflection.

1) 4-$O_2NC_6H_4CONHC_6H_4OH$-p,
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-p,
3) 4-$O_2NC_6H_4CONHC_6H_4N(CH_3)_2$-p,
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-p.

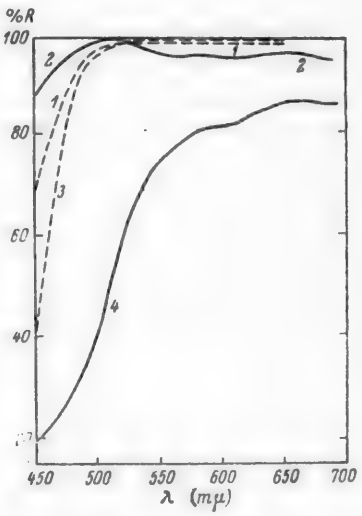


Fig. 5. Curves of light reflection.

1) 4-$O_2NC_6H_4CONHC_6H_4OCH_3$-m,
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OCH_3$-m,
3) 4-$O_2NC_6H_4CONHC_6H_4OCH_3$-p,
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OCH_3$-p.

maximum and blends with the third absorption band applicable to the meta- isomers. The latter appears to a clearly shown extent for compounds with the m-$N(CH_3)_2$ group, but only as a slight projection for compounds with the m-OH group.

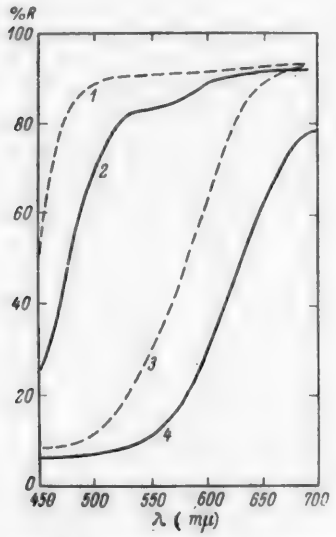


Fig. 6. Curves of light reflection.
1) 4-$O_2NC_6H_4CONHC_6H_4OH$-m
2) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-m
3) 4-$O_2NC_6H_4CONHC_6H_4N(CH_3)_2$-m
4) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-m

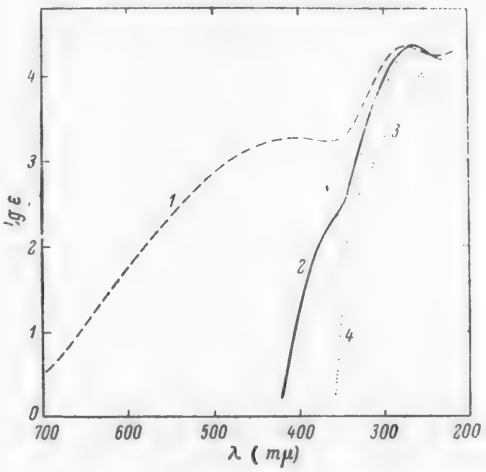


Fig. 7. Light absorption curves.
1) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-p
2) curve of total absorptions 3 and 4,
3) 2,4-$(O_2N)_2C_6H_3CONH_2$,
4) $CH_3CONHC_6H_4N(CH_3)_2$-p.

The curves of compounds containing the p-OCH_3 and the m-OCH_3 groups differ very markedly from the curves of the corresponding hydroxy-derivatives: in the upper part they are practically completely coincident, and only in the lower part of the curve of the compound with the OCH_3 group is it displaced somewhat toward the shorter waves as compared with the curve of the corresponding hydroxy-derivative (for example, with log ϵ = 1 this displacement represents 10 mμ).

Comparison of the absorption curves of the compounds in question with those constructed on the basis of the total absorptions of the individual components, containing analogous electron-acceptor [2,4-$(O_2N)_2C_6H_3CONH_2$] and electron-donor ($CH_3CONHC_6H_4A$) systems, shows that, between these, there is a considerable difference, especially in the case of compounds with the electron-donor group in the para- position (Cf. Figs. 7-9). This essentially distinguishes the nitrobenzoic acid derivatives from the corresponding derivatives of dinitrophenylacetic, dinitrohydrocinnamic, and dinitrophenylbutyric acids, the absorption curves of which proved to be very similar to those constructed for the total absorption of the corresponding selected components. The most marked difference in the absorption curves of the dinitrobenzoyl derivatives from those of the corresponding derivatives of dinitrophenylacetic acid, as also from the summating curves, is to be found in the considerable bathochromic displacement of the boundary of the absorption curve in the visible part of the sepectrum; where, as a rule, this displacement is much greater with compounds containing the electron-donor group (A) in the para- position, and especially with compounds having the p-$N(CH_3)_2$ group. Thus, for example, the absorption boundary, with log ϵ = 1 of the dinitrobenzoyl derivative containing the OH-group in the para- position, has a bathochromic displacement — as compared with the absorption boundary of the corresponding dinitrophenylacetyl derivative — of 53 mμ; while the compound containing the n-OCH_3 group shows 48 mμ. With compounds having the same groups in the meta- position this displacement is respectively only 16 and 12 mμ. With the presence in the compound of the p-$N(CH_3)_2$ group displacement of the absorption boundary reaches the value of 76 mμ. In compounds with the m-$N(CH_3)_2$ group it is again much less (37 mμ with log ϵ = 1.5).

The presence in the dinitrobenzoyl derivatives of considerable absorption in the visible part of the spectrum,

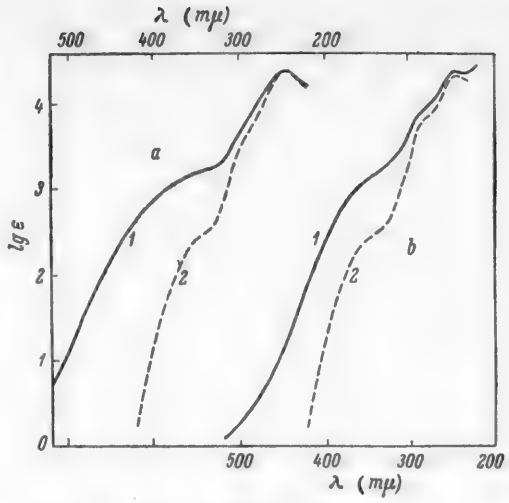


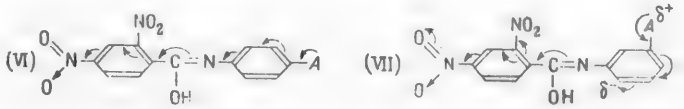
Fig. 8. Light absorption curves.
1, a) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-p; 2, a) Curves of total absorptions of 2,4-$(O_2N)_2C_6H_3CONH_2$ + + $CH_3CONHC_6H_4OH$-p;
1, b) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4OH$-m;
2, b) Curve of total absorptions of 2,4-$(O_2N)_2C_6H_3CONH_2$ + $CH_3CONHC_6H_4OH$-m

even in strongly dilute solutions, may be regarded as evidence of the fact that interaction between electron-acceptor and electron-donor systems in the given case may be effected, no only intermolecularly through exomolecular forces, as with dinitrophenylacetyl derivatives, but also intramolecularly along the chain. Such a possibility is to be found in connection with the capacity of the CONH group for tautomeric (III) and electromeric conversion (IV).

Statements in the literature refer to the possibility that tautomerization of the CONH group takes place in different cases. In work [4], associated with study of the color phenomena with nitrobenzoyl derivatives of aromatic amines, the matter was discussed in detail. The conclusion was reached that, although the possibility of isomerization of the CONH group in the given case was not ruled out, its presence is not necessarily a condition for the color effects with nitrobenzoyl derivatives.

In one of our previous communications [5] it was shown that the N-methyl derivative of N-(4-nitrobenzoyl)-p-aminophenol, where isomerization of the group $CON(CH_3)$ was not possible, has a light absorption curve markedly differing from the absorption curve of the nonmethylated product, and at the same time very similar to the absorption curves of the nonmethylated derivatives of p-nitrophenylacetic, p-nitrohydrocinnamic, and p-nitrophenylbutyric acids. Since displacement of the electron couple of the nitrogen atom is possible also with the N-methylated product, this led us to conclude that the difference in absorption curves referred to is due in fact to a tautomeric conversion of the CONH group, and that, therefore, this latter occurs in solutions of nitrobenzoyl derivatives. A similar conclusion was arrived at by Ramart-Lucas and Wohl [6], as established by comparing the absorption spectra of acetylarylamides of the general formula $CH_3CONHC_6H_4A$ (A = H, o-CH_3, p-CH_3) with the absorption spectra of the corresponding N-methylated products.

The marked difference between the absorption curves of the dinitrobenzoyl derivatives and their corresponding summated curves, and in like manner also differing from the absorption curves of the dinitrophenylacetyl derivatives, gives ground for supposing that also in this case tautomerization of the CONH group takes place. In connection with this the formation of a conjugated chain of double bonds is naturally expressed more strongly in the light absorption curves in the case where the electron-donor group is in the para-position, since, in such case, the electron-acceptor (NO_2) and electron-donor groups appear at the ends of the conjugated chain which also acts as a conductor of electronic displacements towards the nitro groups* (VI).



With the presence of the electron-donor group (A) in the meta-position this latter is not the end of the continuous conjugated chain, and electron displacement from this group along the chain is impossible. Therefore interaction of the electron-donor with the electron-acceptor system in the given case may be effected either directly through exomolecular forces (and tautomerization of the CONH group will appear here only as a modifying

* It was not possible for us, unfortunately, to obtain the 2,4-dinitrobenzoyl derivative of the N-methyl-p-aminophenol. The reaction product of 2,4-dinitrobenzoyl chloride with methyl in an aqueous benzene medium (in the presence of sodium bicarbonate), on separation from the liquid, quickly changed into a resinous mass.

agency), or through an inductive effect which this system will exert on electron displacements along the chain, due to the nitro group through the existence of a high electron density at the carbon atom disposed in the ortho-position in respect to the NH group (VII). In this way, it seems to us, the smaller difference may be explained between the absorption curves of the dinitrobenzoyl derivatives, containing the electron-donor group in the meta-position, and the corresponding total curves, as compared with the para- isomers (Cf. Figs. 7 and 9).

If the sequence of the relative position of the absorption curves of the dinitrobenzoyl derivatives [p-$N(CH_3)_2$, m-$N(CH_3)_2$, p-OH, p-OCH_3, m-OH, m-OCH_3], be compared in most cases it corresponds to the sequence of changes in visible coloring of compounds in the solid state. Some anomaly may be seen only in the compounds with the p-OH group which, in the solid state, is of lighter color than the compound having the n-OCH_3 group; although the latter, as is known, is a weaker electron-donor than the OH, and the absorption curve of the compound with the OCH_3 group is of more hypsochromic form. With dinitrophenylacetyl derivatives, as also with those of dinitro-hydrocinnamic and dinitrophenylbutyric acids, a lack of conformity between the relatively deep coloring in the solid state and in solution is observed as a rule. The following example may serve as a very clear illustration of such a difference: the dinitrophenylbutyryl derivative containing the p-$N(CH_3)_2$ group, as also the corresponding dinitrobenzoyl derivative, are colored a deep red, nearly black; where, as may be seen from the light reflection curves (Fig. 10), the color of the first compound is already somewhat deeper than the second. But the light absorption curve of the dinitrophenylbutyryl derivative (Fig. 11) very markedly differs from the absorption curve of the dinitrobenzoyl derivative, both in the absence of a clearly marked long-wave maximum and in the very considerable hypsochromic displacement of boundaries of the absorption curve in the visible part of the spectrum. This difference in the color state of a substance in the solid form and in solution with dinitrophenyl-butyryl derivatives, as also with those of dinitrohydro-cinnamic and dinitrophenylacetic acids, may be regarded as confirmation of the fact that, with all these compounds, the fundamental factor in coloring is exomolecular reaction between electron-acceptor and electron-donor systems, which may be completely effected only with substances in the solid state, and but partially when in solution. The absence of such a difference with most of the dinitrobenzoyl derivatives indicates that, in the given case, this reaction is achieved also intramolecularly along the chain.

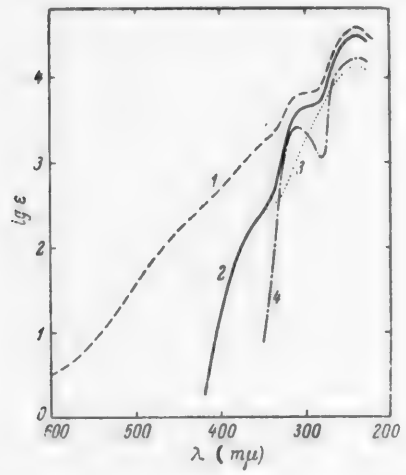


Fig. 9. Light absorption curves
1) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-m,
2) Curve of total absorption 3 and 4,
3) 2,4-$(O_2N)_2C_6H_3CONH_2$,
4) $CH_3CONHC_6H_4N(CH_3)_2$-m.

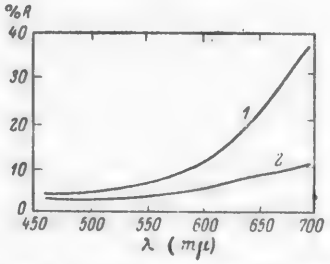


Fig. 10. Light reflection curves.
1) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-p,
2) 2,4-$(O_2N)_2C_6H_3(CH_2)_3CONHC_6H_4N(CH_3)_2$-p.

Figs. 7 and 9, on which, besides the curves of the dinitrobenzoyl derivatives and the total curves corresponding thereto, are given also the curves of the individual components used in constructing the total curves, enable a conclusion to be drawn as to the origin of the absorption bands for the compounds in question. A short-wave band is obviously the result of a superposing of two separate bands corresponding to the electron-acceptor and electron-donor systems. In the case of compounds with the para-electron-donor group, as also of the corresponding total curves, this band is characterized by one well-defined maximum. With compounds containing the meta-electron-donor group there can be noted also a second, though more weakly expressed, maximum, corresponding to the second maximum of the amino component (Fig. 9). A wide long-wave band, that distinguishes the absorption

curves of the dinitrobenzoyl derivatives from the corresponding total curves, is evidently associated with the presence of a common conjugated chain formed by tautomerization of the CONH group.

Effect of introduction of the second nitro group on light absorption in solution. Introduction of the second nitro group into the molecule of a p-nitrobenzoyl derivative is indicated in a bathochromic displacement of the light absorption curve. In order to express the magnitude of this displacement we use figures corresponding to displacement of the absorption boundary when log ϵ = 1. Maximum bathochromic bending of the absorption curve is observed with the introduction of the NO_2 group into a compound containing the strongest electron-donor group $N(CH_3)_2$, namely – 46 mμ with introduction into the para-position and 43 mμ for the meta-position. With the presence of the OH- or OCH_3- group this displacement is considerably less: 17 and 7 mμ for compounds with the OH- group, 21 and 11 mμ for those with the OCH_3- group. But in all these cases, with the introduction of the second NO_2- group, a bathochromic effect is observable. As was noted above, the visible coloring of the dinitrobenzoyl derivatives is not always deeper than that of the corresponding mononitro derivatives, with the presence in the compound of the p-OH or m-OCH_3 group the converse picture is to be seen; that is to say, the mononitro derivatives appear with deeper colorings than the corresponding dinitro compounds. This is confirmed also by the reflection spectra. So we have here a divergence between the relative depth of color of a substance in the solid state and in solution. The reason for this divergence, in the present case too, is evidently to be sought in the complexity of the conditions that cause light absorption: with the dinitrobenzoyl derivatives interaction between electron-acceptor and electron-donor systems may occur not only along the chain but also with the aid of exomolecular forces.

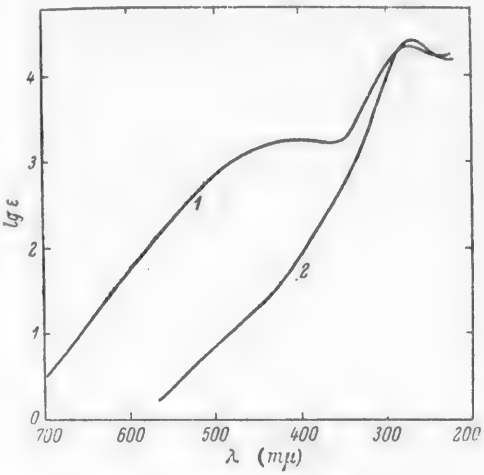


Fig. 11. Light absorption curves.
1) 2,4-$(O_2N)_2C_6H_3CONHC_6H_4N(CH_3)_2$-p,
2) 2,4-$(O_2N)_2C_6H_3(CH_2)_3CONHC_6H_4N(CH_3)_2$-p.

It is, moreover, interesting to note that the introduction of the second NO_2 group into the molecule of the p-nitrophenylacetyl derivatives produces a much stronger bathochromic displacement of the absorption curves than the introduction of the same group into the analogous p-nitrobenzoyl derivatives: on an average from two to three times stronger, and in the presence of the m-OH group even five times. The explanation for this, it seems to us, is to be sought in the possibility that the strengthening of the electron-acceptor system BK through the second NO_2 group leads to a considerable increase in the complex-forming abilities of this system, i.e. the ability to enter into direct interaction, through the exomolecular forces, with the electron-donor system; and therefore even in a solution this interaction proceeds further than when only one NO_2 group is present in the compound. Since with both nitro- and dinitrophenylacetyl derivatives this interactivity is a principal factor governing the coloring of compounds, it is natural that its strengthening in this case is shown on the absorption curves more markedly than is the case with dinitrobenzoyl derivatives where interaction between chromophoric systems may be effected also intramolecularly along the chain.

As a result of the more vigorous bathochromic action occasioned by the introduction of the second NO_2 group into the molecule of the p-nitrophenylacetyl derivative, as compared with introduction of the same group into the molecules of the p-nitrobenzoyl derivative, is the fact that, in the transition from the dinitrophenylacetyl derivatives to the corresponding dinitrobenzoyl derivatives, in all cases less bathochromic bending of the absorption curve is observed than in the transition from the analogous p-nitrophenylacetyl derivatives to those of p-nitrobenzoic acid. In other words, the absorption curves of the dinitrobenzoyl and dinitrophenylacetyl derivatives, as regards their position, differ from each other less than do the absorption curves of the analogous mononitro derivatives.

In regard to the positions of the maxima, the short wave maximum, as a rule, with introduction of the second NO_2 group into the p-nitrobenzoyl derivative, experiences a slight hypsochromic displacement (4-8 mμ). Exceptions are to be found in compounds with the $N(CH_3)_2$ group, where, with the introduction of the second NO_2 group, the maximum is either not displaced at all [as with the m-$N(CH_3)_2$], or undergoes a slight bathochromic displace-

ment [as with the p-$N(CH_3)_2$]. The long wave maximum, with all compounds containing the electron-donor group in the meta- position, is displaced bathochromically when the second NO_2 group is introduced. With the presence in the compound of the electron-donor in the para- position the bathochromic effect is observed only in compounds with the $N(CH_3)_2$ group; in the case of those with the OH and OCH_3 groups a hypsochromic effect is to be seen. All these phenomena likewise require of course explanations that, at the present moment, can only be given with difficulty.

EXPERIMENTAL

2,4-Dinitrobenzoic acid was obtained from 2,4-dinitrotoluene by oxidation with potassium permanganate [7]; the chloride, by the action of phosphorus pentachloride [8]. The dinitrobenzoyl derivatives were produced by the action of the acid chloride on the corresponding amine in an aqueous-benzene medium in the presence of sodium bicarbonate, similarly to the mononitrobenzoyl derivative described earlier [4].

3-(2',4'-Dinitrobenzamino)-anisole (Table 1, No. 1). The reaction product was twice recrystallized from alcohol. Pale yellow crystals were obtained of parallelepiped form, with m.p. of 172.5-173.5°; easily soluble in acetone, fairly easily in alcohol, less easily in benzene, and difficultly in ether.

Found %: N 13.43. $C_{14}H_{11}O_6N_3$. Calculated %: N 13.25.

4-(2',4'-Dinitrobenzamino)-anisole (Table 1, No. 2). After recrystallizing twice from alcohol yellow crystals were obtained in the form of rectangular flakes, with m.p. of 201-202°. They were easily soluble in acetone, less easily in alcohol, and difficultly in benzene and ether.

Found %: N 13.49. $C_{14}H_{11}O_6N_3$. Calculated %: N 13.25.

3-(2',4'-Dinitrobenzamino)-phenol (Table 1, No. 3). Recrystallized twice from alcohol; yellow fine crystalline precipitate, with m.p. of 119.5 to 120.5°; easily soluble in acetone, fairly easily in alcohol, difficultly in benzene and ether.

Found %: N 13.79. $C_{13}H_9O_6N_3$. Calculated %: N 13.86.

4-(2',4'-Dinitrobenzamino)-phenol (Table 1, No. 4). The reaction product was recrystallized twice from dilute alcohol with addition of carbon. Yellow crystals were obtained of m.p. 212.5-213°, with approximately the same solubility in organic solvents as the preceding.

Found %: N 13.98. $C_{13}H_9O_6N_3$. Calculated %: N 13.86.

N,N-Dimethyl-N'-(2,4-dinitrobenzoyl)-m-phenylenediamine (Table 1, No. 5). Recrystallized twice from alcohol; dark red flaky crystals of m.p. 201.5-202°; easily soluble in acetone, less easily in alcohol, difficultly in benzene, still more difficultly in ether. From benzene the substance separates out in bright or lustrous form, of orange-red color, crystallizing in the form of small needles with the same m.p. as the dark red form.

Found %: N 17.04. $C_{15}H_{14}O_5N_4$. Calculated %: N 16.97.

N,N-Dimethyl-N'-(2,4-dinitrobenzoyl)-p-phenylenediamine (Table 1, No. 6). The reaction product was recrystallized from acetic acid and then from acetone alcohol mixture. Flaky crystals were obtained of a deep red color, nearly black, of m.p. 240.5-241° (with decomposition). (M.p. depends somewhat on the rate of heating). The substance is fairly easily soluble in acetone and acetic acid, less easily in alcohol, and difficultly in benzene and ether.

Found %: N 17.34. $C_{15}H_{14}O_5N_4$. Calculated %: N 16.97.

Spectroscopic measurements: The absorption spectra were measured with the Beckmann spectrophotometer. Alcohol (rectified) and acetone were used as solvents. Both of these were previously distilled with a fractionating column, and the acetone afterwards dried over potash. In alcohol more dilute solutions were prepared (10^{-3} and 10^{-4} M) and in the acetone, more concentrated ($0.5 \cdot 10^{-2}$ M). The reflection spectra were measured with apparatus described in the atlas [9]. Details of the measurements were given by us earlier [10].

SUMMARY

1. A series of arylamides of 2,4-dinitrobenzoic acid of general formula (I) were synthesized, where

A = OCH_3, OH, $N(CH_3)_2$ in the meta- or para- positions in respect to the NH group, and their absorption and reflection spectra were measured.

2. All the synthesized compounds were colored, and those with the strongest electron-donor group p-$N(CH_3)_2$ had a deep red, nearly black, color. The reflection curves obtained, confirmed and in some cases also gave greater precision to the visual observations.

3. The absorption curves obtained for the dinitrobenzoyl derivatives differed markedly from those for the corresponding arylamides of the 2,4-dinitrophenylacetic, 2,4-dinitrohydrocinnamic, and γ-(2,4-dinitrophenyl)-butyric acids, and also from the curves constructed on the basis of the total absorptions of the respective components ($2,4\text{-}(O_2N)_2C_6H_3CONH_2 + CH_3CONHC_6H_4A$). This is regarded as a fact indicating that, in the dinitrobenzoyl derivatives, interaction between electron-acceptor and electron-donor systems, governing the color of the compounds, may be effected not only with the aid of exomolecular forces, but also along the chain, owing to tautomerization of the CONH group and formation of a continuous conjugated chain of double bonds.

4. Introduction of the second NO_2 group into the molecule of p-nitrobenzoyl arylamides, as a rule, produces less bathochromic effect than does introduction of the same group into the molecule of the p-nitrophenylacetyl arylamides. This again is associated with the possibility, in the former, of chain interaction.

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CHEMISTRY OF THE NITRO-OLEFINS

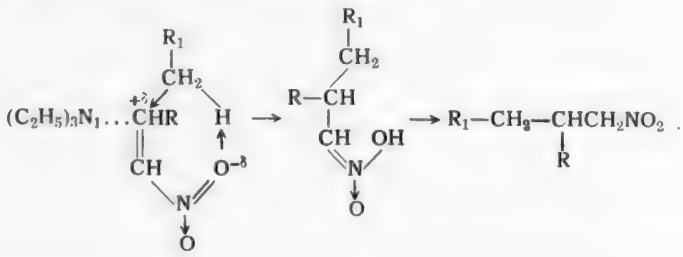
II. REACTION OF NITRO-OLEFINS WITH SUBSTANCES HAVING ACTIVE METHYL GROUPS *

V. V. Perekalin and A. S. Polyanskaya

Reactions of the nitro-olefins with substances containing active hydrogen atoms in the methine, methylene, and methyl groups, open up wide possibilities of obtaining by simple methods various practically important classes of organic substances: polynitro compounds, polyamines, amino acids [1-3].

If the reaction of unsaturated nitrocompounds with substances having active methylene groups has occupied several researchers [1, 4], and reaction with active methine components has been described only in individual cases [5-7], then the condensation of nitro-olefins with compounds having active methyl groups has received practically no attention [8, 9].

We have for the first time effected reactions of the nitro-olefins of the aliphatic, aromatic, and heterocyclic series (nitroisohexylene, nitrostyrene, furylnitroethylene) with a series of active methyl components (mesomethylacridine, iodomethylates, of quinaldine and methylbenzthiazole).



where R is alkyl, aryl, heterocyclo, R_1 is an electrophil radical conjugated with a methyl group.

Other substances containing methyl groups activated with heteroatoms (2,4-dinitrotoluene, α-picoline and its iodomethylate, quinaldine, methylbenzthiazole, methylbenzimidazole, methylbenzoxazole, and the iodomethylates of the two latter) were not reacted with the nitro-olefins.

The reaction products (Table 1) are the result of interaction only of equimolecular amounts of nitro-olefins and methyl components. It was not possible to effect the condensation of two or three moles of nitro-olefins (as in the case of acronitrile) with a mole of the methyl component. The reaction of nitroisohexylene with mesomethylacridine led to formation of two isomeric compounds (IV-α and IV-β); but the question of their structural differences has so far remained undecided. A similar kind of stereochemical isomers was found also in studying the interaction of nitrostilbene with malonic ester [10].

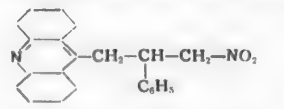
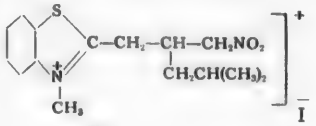
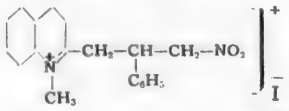
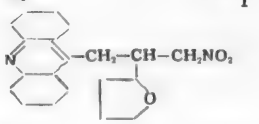
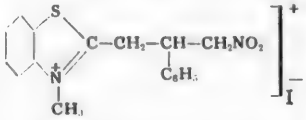
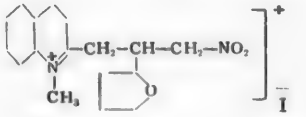
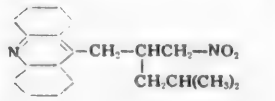
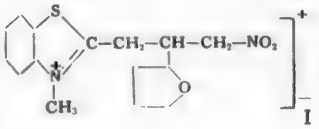
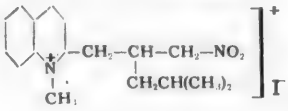
The syntheses proceeded preferably in the presence of basic catalysts(triethylamine) with heating of the initial substances in organic solvents (benzene, methanol), or with short-period melting (condensation of mesomethylacridine with nitroisohexylene and furylnitroethylene).

Based on approximate comparisons of yields of reaction products the nitro-olefins may be disposed in fairly

* For Part I see (Original Russian pagination. See C. B. Translation) J. Gen. Chem. 24, 513 (1954).

accurate order according to decreasing activity: furylnitroethylene, nitrostyrene, nitroisohexylene.

TABLE 1

№	Formula	№	Formula
(I)		(VI)	
(II)		(VII)	
(III)		(VIII)	
(IV)		(IX)	
(V)			

Of the methyl components the most active in the given reaction is mesomethylacridine; it condensed with nitro-olefins without the aid of a catalyst. Nevertheless the use of a catalyst is a governing condition for the successful reaction of the tested nitro-olefins with methyl components. (In the case of mesomethylacridine a catalyst also reduces reaction time and increases yield).

The amount of catalyst used has no appreciable affect on the course of the reaction.

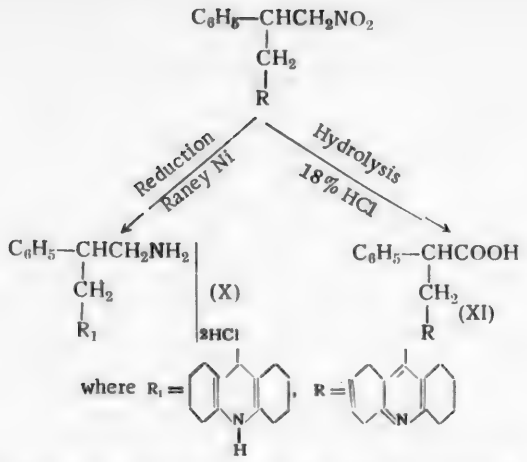
An important part in effecting this reaction between the nitro-olefins and methyl components is played by catalyst basicity. Toward weak bases (K_b 10^{-9} to 10^{-10} and lower) the reacting substances remain indifferent. Stronger bases (K_b 10^{-3} and over) cause a preferential polymerization of the nitro-olefin, and only catalysts of medium basicity (K_b 10^{-4} to 10^{-5}) favorably affect the course of the desired reaction.

Polar solvents — methanol and to a lesser degree acetone — cause polymerization of the olefin. Thus, a sample of furylnitroethylene dissolved in benzene, in the presence of piperidine and diethylamine, remained unaffected during 5 days; but in methanol, with this catalyst, it was quantitatively polymerized.

Study of the chemical properties of the synthesized products was not part of the present program; yet, by way of example, conversion of the condensation product of nitrostyrene with mesomethylacridine (II) into the corresponding amine (X) and carboxylic acid (XI) was undertaken.

The reaction of nitro-olefins with active methyl (methylene, methine or methenyl) components is undertaken as a type of the well-studied reactivity of the latter with compounds having active double bonds (acronitriles, acrylates, vinyl ketones etc.)

It may be suggested that the reaction proceeds through formation of a reaction complex which is stabilized in the end product as a result of addition 1-4 of the methyl component to the nitro-olefin (see scheme); the hydrogen atoms of its methyl group are activated by conjugation with the hetero-atom entering into its composition, and the reactivity of the olefin is determined by conjugation of the double bond with the nitro-group.



The catalyst, activating the nitro-olefin in the first place,* stabilizes the electron gap in the carbon atom of its ethylene radical, and favors polarization of the double bond.

The extent of polarizability of the nitro-olefin (and accordingly also its activity) increases with catalyst basicity; in the presence of highly basic catalysts the rate of its polymerization increases the rate of reaction with the methyl component; with catalysts of medium (optimum) basicity the polymerization velocity is reduced, and reaction of the nitro-olefins with the methyl (methylene, methine) component begins to predominate.

EXPERIMENTAL

1-(9'-Acrylyl)-2-phenyl-3-nitropropane (I). A solution of 0.64 g mesomethylacridine and 0.49 g nitrosyrene in 30 ml benzene was boiled 5 hrs and poured into the crystallizer. The precipitate, separated after the solvent was evaporated, was washed with benzene. (I) was in the form of small white crystals, m.p. 164.5° (from dichlorethane), easily soluble in acetone and pyridine, and, with heating, also in the usual organic solvents; in hydrochloric and sulfuric acids, with yellow fluorescence. Yield 0.59 g (52%).

Iodo-1-[2'-(N-methyl)-quinolyl]-2-phenyl-3-nitropropane (II). 1.49 g nitrostyrene was dissolved in 30 ml benzene; 2.85 g quinaldine iodomethylate and 3 drops TEA (triethylamine) were added. The suspension was boiled with vigorous stirring for 8 hrs, the condensation product cooled and filtered off, slightly contaminated with quinaldine iodomethylate. (II) was in the form of yellow crystals, m.p. 174.5° (from methanol); soluble in hot water. Yield 4.2 g (96 %).

Iodo-1-[2'-(N-methyl)-thiazyl]-2-phenyl-3-nitropropane (III). 3 drops TEA was added to a solution of 1.49 g nitrostyrene and 2.9 g methylbenzthiazole iodomethylate in 100 ml anhydrous methanol, and boiled for 4 hrs. Crystals, separating after the solvent was driven off, were washed with acetone. (III) was in the form of small white stars, m.p. 171.5° (from methanol); soluble in methanol, ethanol, pyridine and hot water; difficultly in dichlorethane and acetone. Yield 2.3 g (52 %).

α and β forms 1-(9'-acridyl)-2-isobutyl-3-nitropropane (IV-α and IV-β). 2 drops TEA was added to a solution of 3.86 g mesomethylacridine and 3.87 g nitroisohexylene [11] in 50 ml ethanol at room temperature. Within 24 hrs 2.4 g of the condensation product (IV-β) was filtered off, m.p. 148°. A further 1.05 g of substance (IV-α), m.p. 148-170° was separated from the filtrate after evaporating down to one-third of its original volume.

(IV-β) were long yellowish needles, m.p. 149° (from ethanol); easily soluble in acetone, dichloroethane, pyridine, and, with heating, also in benzene, toluene, methanol, ethanol; in concentrated sulfuric and hydrochloric acids, a greenish yellow fluorescence appears.

(IV-α) was at first recrystallized from a small quantity of ethanol (m.p. 173-178°), and then repeatedly

* It is not to be overlooked that the catalyst may increase the mobility of the hydrogen atoms of the methyl component through establishing the hydrogen bond.

from acetone, m.p. 195°; fine yellowish needles; soluble in ethanol, and, with heating, in acetone, dichloroethane pyridine; in concentrated hydrochloric acid there was yellowish fluorescence. Total yield 3.45 g (53 %).

The total yields by melting in the presence of TEA and heating in ethanol without catalyst were respectively 30 % and 10 % of theoretical.

Iodo-1-[2'-(N-methyl)-quinolyl]-2-isobutyl-3-nitropropane (V). A solution of 0.65 g nitroisohexylene and 1.44 g quinaldine iodomethylate in 30 ml anhydrous methanol, containing 2 drops TEA, was heated for 5 hrs at 30° and for 12 hrs at room temperature; the solvent was evaporated and the precipitate washed with ethanol. (V) in the form of lemon-yellow crystals, m.p. 178° (from methanol); soluble in methanol, ethanol, pyridine, and hot water; rather difficultly in acetone, chloroform, and dichlorethane. Yield 1.3 g (62 %).

Iodo-1-[2'-(N-methyl)-thiazyl]-2-isobutyl-3-nitropropane (VI). 1 g nitroisohexylene and 1.47 g methylbenzthiazole iodomethylate were dissolved in 20 ml anhydrous methanol, 2 drops TEA added, and boiled for 6 hrs. A crystalline condensation product gradually separated from the resins remaining after the solvent had been evaporated. (VI) was in the form of small white crystals, m.p. 153° (from ethanol); soluble in methanol, ethanol, acetone, dichloroethane, pyridine, and hot water. Yield 1.22 g (57 %).

1-(9'-Acridyl)-2-furyl-3-nitropropane (VII). A solution of 2.78 g furylnitroethylene [12], 3.86 g mesomethylacridine, 2 drops TEA, in 200 ml benzene was boiled for 5 hrs. The resin forming after the solvent had been driven off was gradually transformed into dark brown velvety crystals that were washed with methanol. (VII) was in the form of yellowish crystals, m.p. 168° (from benzene); easily soluble in acetone and dichloroethane and, with heating, in methanol, ethanol, benzene; in concentrated sulfuric and hydrochloric acids there was greenish-yellow fluorescence. Yield 4.38 g (66 %).

When held for 24 hrs in ethanol at room temperature in the absence of a catalyst the yield was 68 %. When melted in the presence of TEA the yield of (VII) was 44 %.

Iodo-1-[2' (N-methyl)-quinolyl]-2-furyl-3-nitropropane (VIII). 2.85 g quinaldine iodomethylate and 3 drops TEA were added to a solution of 1.39 g furylnitroethylene in 30 ml benzene, the suspension boiled for 1 hr, and, on cooling, the condensation product was filtered off. (VIII) was in the form of light brown crystals, m.p. 161° (from ethanol); easily soluble in acetone, dichloroethane and pyridine, hot water; difficultly in chloroform. Yield 3.25 g (76 %).

Holding for 24 hrs at room temperature increases yield to 84 %.

Iodo-1-[2'-(N-methyl)-thiazyl]-2-furyl-3-nitropropane (IX). A suspension of 2.91 g methylbenzthiazole iodomethylate in 30 ml benzene, containing 1.39 g furylnitroethylene and 3 drops TEA, was boiled with stirring for 4 hrs. After 12 hrs standing at room temperature the precipitate was filtered off. (IX) formed light brown crystals, m.p. 163.5° (from methanol) easily soluble in methanol, ethanol, pyridine, and hot water; difficultly in dichloroethane and acetone. Yield 3.7 g (86 %).

1-(9'-dihydroacridyl)-2-phenyl-3-amino propane hydrochloride (X). 0.85 g Raney nickel catalyst in 30 ml methanol was saturated with hydrogen under vigorous stirring, 0.85 g of product (I) was added, and the mixture hydrogenated at room temperature. Within 6 hrs after absorption of 235 ml hydrogen hydrogenation was completed (for hydrogenating the nitro group and the double bond of the acridine ring 222 ml hydrogen is required).

The catalyst was removed by filtering and the product, washed with methanol. The filtrates were combined and concentrated. The transparent resinous residue was dissolved in dilute hydrochloric acid, and within 24 hrs the separating amine hydrochloride was filtered. (X) forms an amorphous lemon-yellow powder, m.p. 288° (reprecipitating with acetone from methanol); easily soluble in methanol, ethanol; aqueous solutions have a greenish yellow fluorescence. Yield 0.4 g (45 %).

1-(9'-Acridyl)-2-phenyl-3-propanoic acid (XI). 3.42 g of (II) was boiled and stirred for 6 hrs with 100 ml of 18 % hydrochloric acid; after cooling the orange-colored residue was filtered off. (XI) forms a light yellow powder, m.p. 255° (from mixed ethanol-pyridine). It is soluble in pyridine, glacial acetic acid, and, with heating, in a 10 % sodium carbonate solution. The sodium salt forms white silky needles. Its aqueous solution in the ultraviolet has a clear blue fluorescence. Yield 2.8 g (86 %).

Analysis results are given in Table 2.

TABLE 2

Substance	Found %					Formula	Calculated %					Mol. wt.	
	C	H	N	S	J		C	H	N	S	J	Found	Calc.
(I)	77.31 77.47	5.56 5.67	8.27 8.37	— —	— —	$C_{22}H_{18}O_2N_2$	77.19	5.30	8.18	—	—	358, 358	342.3
(II)	52.82 52.63	4.57 4.54	6.40 6.66	— —	29.15 29.54	$C_{19}H_{19}O_2N_2I$	52.57	4.41	6.49	—	29.23	—	—
(III)	46.25 46.48	3.84 4.09	6.28 6.33	7.38 7.57	29.14 29.04	$C_{17}H_{17}O_2N_2SI$	46.39	4.12	6.36	7.26	28.83	—	—
(IV-α)	74.91 74.63	7.01 7.14	8.67 8.69	—	—	$C_{20}H_{22}O_2N_2$	74.57	6.87	8.68	—	—	334, 322 324	322.4
(IV-β)	74.65 74.56	7.23 7.28	8.94 8.99	— —	— —								
(V)	49.71 49.54	5.74 5.63	6.74 6.47	—	30.68 30.61	$C_{17}H_{23}O_2N_2I$	49.29	5.59	6.75	—	30.64	—	—
(VI)	42.83 42.99	5.65 5.35	6.82 6.78		30.04 30.09	$C_{15}H_{21}O_2N_2SI$	42.87	5.03	6·66	7.63	30.20	— —	—
(VII)	72.11 72.15	4.82 5.02	8.44 8.38	—	—	$C_{20}H_{16}O_3N_2$	72.27	4.88	8.42	—	—	338, 364	332.4
(VIII)	48.06 47.89	4.26 4.36	6.41 6.54	—	—	$C_{17}H_{17}O_3N_2I$	48.14	4.04	6.60	—	29.92	—	—
(IX)	41.79 42.03	3.48 3.54	6.53 6.35	7.42 7.11	29.60 29.28	$C_{15}H_{15}O_3N_2SI$	41.88	3.51	6.51	7.43	29.50	—	—
(X)	— —	— —	7.02 7.03	— —	— —	$C_{22}H_{23}N_2Cl_2$	—	—	7.33	—	—	—	—
(XI)	— —	— —	4.21 4.72	— —	— —	$C_{22}H_{17}O_2N_2$	—	—	4.29	—	—	—	—

SUMMARY

1. It was established for the first time that nitro-olefins, preferably in the presence of basic catalysts, react with active methyl components.

2. It was shown that the reaction described is of a general character and provides a method of introducing the nitroethyl group combined with different alkyl, aryl, and heterocyclic radicals, into compounds having an active methyl group.

3. The possibility of converting the condensation products into the corresponding amines and carboxyl acids was noted.

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THE ALKYLATION OF NAPHTHALENE WITH ISOALCOHOLS IN THE PRESENCE OF BF_3

I. A. Romadan

Many works are known relating to the preparation and study of alkylnaphthalenes with normal radicals. Only in recent years works have been published by English and American chemists [1] who have prepared and characterized a number of monoalkylnaphthalenes containing radicals in the 1 and 2 positions. There are, however, few works in which alkylnaphthalenes with iso- and tertiary radicals have been described with sufficient accuracy. Thus 1-isobutylnaphthalene [2], 1,4-ditert-butylnaphthalene [3], 1-isopropylnaphthalene and 1-isobutylnaphthalene [4] are known. In a previous communication it was shown that naphthalene is readily alkylated by the molecular compounds of normal alcohols with boron trifluoride at 165-170°; this leads to the formation of oily material in good yield.

This work describes the alkylation of naphthalene with isopropyl, isobutyl and isoamyl alcohols. The mono- and dialkylnaphthalenes have been obtained in yields of 90-98 % calculated on the original naphthalene. Individual substances have been isolated using a vacuum column with an efficiency of 48-50 theoretical plates, part of these individual stubstances being crystalline with sharp melting points. It has been shown that the yield of dialkylnaphthalenes depends on the original alcohol and increases on going from isopropyl to isoamyl alcohol. The BF_3 brings about isomerization of the secondary radicals to the tertiary. Thus the alkylation of naphthalene with isoamyl alcohol led to the formation of 1- and 2-tert-amylnaphthalenes, together with 1,4-ditert-amylnaphthalene, m.p. 119.5°, which is not described in the literature. In the reaction with isoalcohols, the intermediate alkylating agents are apparently olefins, formed as a result of the easier removal of water from alcohols of iso-structure by comparison with normal alcohols. It is only via the olefins that 1- and 2-tert-butylnaphthalene, and the 1,4-ditert-butylnaphthalene described in the literature [3], can be formed from isobutyl alcohol. All the crystalline substances obtained contain the radicals in the 1,4- positions, as is proved by oxidation to naphthalene--1,4-dicarboxylic acid. Together with the alkylnaphthalenes, dimers and trimers of the corresponding olefins are obtained in the reaction with the isoalcohols.

EXPERIMENTAL

The molecular compounds of general formula $2ROH \cdot BF_3$ were prepared by the method described earlier [5]. The alkylation of the naphthalene was carried out in a three-necked flask fitted with reflux condenser and mechanical stirrer. The molecular compound was added dropwise with energetic stirring to the naphthalene heated to 165-170°. The BF_3 evolved in the reaction was absorbed in wash bottles containing alcohol and cooled with ice.

The reagents were taken in the ratio of 1 mole of naphthalene to 1.5 moles of alcohol.

Characteristics of the alcohols: isopropyl, b.p. 82-83°, d_4^{20} 0.7883, n_D^{20} 1.3965; isobutyl, b.p. 107-108°, d_4^{20} 0.8032, n_D^{20} 1.3958; isoamyl, b.p. 130°, d_4^{20} 0.8117.

The duration of the reaction was 2.5-3 hours for the isoalcohols, 6-8 hours for the normal alcohols. When the reaction was complete the upper oily layer was removed and steam distilled for 4-6 hours. The steam removed the olefin dimers and the unreacted naphthalene, leaving the alkylnaphthalenes in the distillation flask. The oils were dried and distilled first from a flask over metallic sodium and then on a vacuum column.

The alkylation with isopropyl alcohol led to the formation of 1,4-diisopropylnaphthalene, which is not de-

Specimen No.	Name	Temperature			n_D^{20}	d_4^{20}	Freezing point	M		Found %		Calculated %	
		Boiling point	Boiling point in vacuo (mm)	Melting point				Found	Calc.	C	H	C	H
1	1-Isopropylnaphthalene	267.4°	82.4°(0.7)	—	1.5864	0.9848	—14.7°	171	170	91.68	8.19	91.66	8.29
2	2-Isopropylnaphthalene	268.9	85.5 (0.7)	—	1.5858	0.9788	—5.5	170.4	170	91.98	8.30	91.66	8.29
3	Diisopropylnaphthalene	293	104.3 (0.7)	—	1.5652	0.9509	+7.4	210.7	212	90.47	9.46	90.14	9.86
4	Diisopropylnaphthalene	297	107.1 (0.7)	130.3°	—	—	—	213.1	212	90.44	9.73	90.14	9.86
5	1-Tert-butylnaphthalene	279	70 (0.1)	—	1.5785	0.9715	—11.3	181	184	91.37	8.79	91.25	8.75
6	2-Tert-butylnaphthalene	281.6	73.1 (0.075)	—	1.5757	0.9691	— 5.2	186	184	91.49	8.46	91.25	8.75
7	1,4-Ditert-butylnaphthalene	304—306	108.4 (0.3)	132	—	—	—	242.1	240	90.23	9.74	89.97	10.03
8	1,4-Diisobutylnaphthalene	—	109.8 (0.3)	93	—	—	—	236	240	90.28	9.71	89.97	10.03
9	1-Tert-amylnaphthalene	283	87.5 (0.25)	—	1.5763	0.9672	—7	196	198	90.66	9.35	90.85	9.15
10	2-Tert-amylnaphthalene	287	91 (0.25)	—	1.5732	0.9627	—1.3	201	198	90.74	9.29	90.85	9.15
11	1,4-Ditert-amylnaphthalene	313	114 (0.25)	119.5	Crystals	—	—	268.4	268	89.71	10.15	89.48	10.52

scribed in the literature, together with almost equal quantities of 1- and 2-monoisopropylnaphthalene. Oxidation with potassium permanganate yielded the corresponding naphthalenecarboxylic acids.

The reaction with isobutyl alcohol led to the formation of 1- and 2-tertbutylnaphthalenes; the α--isomer amounted to 58-60%, calculated on the monoalkylnaphthalene. At the same time two crystalline substances were isolated, which distilled together at 304-306°. On prolonged standing the oil first yielded coarse crystals with m.p. 132° (from ethanol) — 1,4--ditert-butylnaphthalene, which is described in the literature [3]. When these crystals had been removed, the oil yielded crystals in the form of long thin needles, interlaced like felt. M.p. 93° (from alcohol). If the oily product is dissolved in alcohol immediately after distillation, then after 3-4 days coarse crystals separate, after which fine needles resembling glass wool are precipitated from the mother liquor. The substances behave differently in their reaction with bromine: the substance with m.p. 93° reacts comparatively readily with bromine in carbon tetrachloride at room temperature. In 1,4-diisobutylnaphthalene substitution by bromine should take place readily thanks to the mobile hydrogen atom on the tertiary carbon atom. Oxidation with potassium permanganate yielded naphthalene-1,4--dicarboxylic acid with m.p. 304° (according to the literature data, 309°).

The reaction with isoamyl alcohol yielded 1- and 2-tert-amylnaphthalenes — oily substances, together with crystalline 1,4-ditert-amylnaphthalene, which crystallizes slowly from methanol and ethanol or directly from the oil after distillation on a vacuum column. This forms coarse crystals with m.p. 119-119.5°. The yield of 1,4-ditert-amylnaphthalene is 36-40 % calculated on the amylnaphthalenes. The results of the studies are given in the Table.

SUMMARY

1. The alkylation of naphthalene by molecular compounds of general formula $2ROH \cdot BF_3$ at high temperatures has been used to prepare, and isolate in good yield, mono- and diisopropyl-, mono- and ditert-butyl-, mono- and ditert-amylnaphthalenes. Among the monoalkylnaphthalenes, the 1-alkylnaphthalenes predominate.

2. The formation of 1- and 2-tert-amylnaphthalenes and 1,4-ditert-amylnaphthalene is caused by the isomerization of the isoamyl radical to the tertiary under the influence of the BF_3.

3. 1,4-Diisopropyl-, 1,4-diisobutyl- and 1,4--ditert-amylnaphthalenes have been prepared for the first time.

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DIPOLAR IONS FORMED BY REMOVAL OF A PROTON FROM THE NH-GROUP

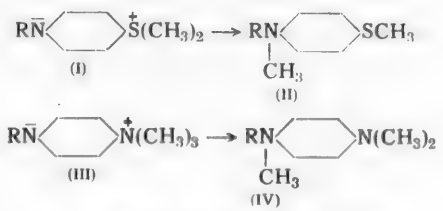
XI. THE REARRANGEMENT OF DIPOLAR IONS OF THE AMMONIUM SERIES

A. M. Simonov and M. N. Okorokova

It has been found earlier [1] that dipolar ions of structure (I) undergo easy rearrangement on melting with the formation of the corresponding N-alkyl-anilides (II). It seemed to us of interest to examine the possibility of such rearrangement in the structurally analogous dipolar ions of the ammonium series. With this aim we synthesized the dipolar ions of structure (III) and studied their behavior on melting.

The dipolar ion (IIIa) was prepared by the action of ammonia on an aqueous solution of the original quaternary ammonium salt with subsequent dehydration of the precipitated betaine hydrate in a desiccator over caustic alkali. The betaine (IIIb), which is of a dark red color, is formed from the corresponding quaternary ammonium salt by the action of caustic alkali alone. Taking into consideration the deep color of the precipitate, which does not change when it is dried, and the inability of the dipolar ion in question to undergo hydration on standing in steam, we may assume that the betaine (IIIb) is formed directly by the action of alkali on the original salt even in aqueous medium. For the structure of dipolar ions of this type see [2, 5].

When heated for a short time above their melting points the dipolar ions obtained, like their sulfonium analogs, undergo isomerization with the formation of N-alkylanilides (IV); the structure of the latter was proved by an alternative synthesis.



For (I)-(IV): (a) $R = NO_2C_6H_4SO_2$,
(b) $R = NO_2C_6H_4CO$.

The change under study normally takes place more smoothly for the compounds of the sulfonium series than for their ammonium analogs. Whereas the dipolar ion (Ia) is completely converted in the molten state to the anilide (IIa), the isomerization of the betaine of the ammonium series (IIIa) is accompanied by the formation of tar, and the yield of anilide (IVa) amounts to only 25%. The observations which we have made agree with the literature data, according to which the sulfonium compounds react more readily then the ammonium compounds in alkylation reactions [3].

Although in the betaines (Ib) and (IIIb) a considerable part of the anionic charge is probably carried by the O-atom of the CO-group, only the N-alkyl derivative is formed in the isomerization. This is evidently caused by a redistribution of the electron density in the reaction process. Indeed, since the betaines are inner quaternary onium salts, and the alkylating agent (the onium group of the betaine) is comparatively weak, we have established, in the change in question, the conditions which, in the lactam–lactim series, according to the views of A. N. Nesmeyanov and M. I. Kabachnik [4], favor the reaction involving transfer of the reactive center, leading to the formation of the N-derivatives.

In conclusion we would mention that we were not able to bring about the rearrangement of the methylbetaine (6-methoxy-8-p-toluenesulfonamidoquinoline) [5].

EXPERIMENTAL

4-(p-Nitrobenzoylamino)-N,N-dimethylaniline methyl-p-toluenesulfonate was prepared from 4-(p-nitrobenzoylamino)-N,N-dimethylaniline [6] and methyl p-toluenesulfonate at 130-140°. Colorless needle-shaped crystals (from methanol) with decomposition temperature lying between 265 and 272° depending on the rate of heating. The addition of ammonia to a warm aqueous solution of the salt caused the solution to turn yellow; the original salt, and not the betaine, precipitated on cooling.

Found %: S 6.74, 6.78. $C_{23}H_{25}O_6N_3S$. Calculated %: S 6.80.

4-(p-Nitrobenzoylamino)-N,N-dimethylaniline methylbetaine (IIIb). 5 ml 2 N caustic potash solution was added to a solution of 1.44 g of the quaternary salt in 10 ml water and 5 ml alcohol. When the orange solution was cooled, dark red crystals were precipitated, filtered off and washed with alcohol and water. The substance did not lose weight when heated in vacuo (70°) after being dried in a desiccator over alkali. Yield 0.67 g (80%). The betaine is very sparingly soluble in pyridine and nitrobenzene, more soluble in hot alcohol; it is precipitated from alcoholic solution with ether; fairly readily soluble in water when heated; the yellow solution deposits the dipolar ion again on cooling; the ion is precipitated more readily by the addition of alkali. When carbon dioxide was passed through a suspension of the betaine in water, a colorless solution was formed. The betaine did not become hydrated when left to stand in a desiccator containing 2 N alkali. The application of heat at first causes considerable darkening of the substance, after which it melts with 2-3° of 170°. When melted rapidly the betaine undergoes isomerization with the formation of p-nitrobenzoyl 4-dimethylamino-N-methylanilide. (4'-dimethylamino-N-methyl-p-nitrobenzanilide).

Found %: N 14.04, 14.39. $C_{16}H_{17}O_3N_3$. Calculated %: N 14.04.

p-Nitrobenzoyl 4-dimethylamino-N-methylanilide. (4'-dimethylamino-N-methyl-p-nitrobenzanilide). a) Preparation by isomerization of 4-(p-nitrobenzoylamino)-N,N-dimethylaniline methylbetaine. 0.90 g of the powdered betaine was placed in a wide test tube which was then immersed in an oil bath heated to 180°. The melt was stirred periodically while the temperature of the oil was raised over a period of 5 minutes to 190° after which heating was continued at this temperature for a further 5 minutes. The transparent dark red melt, which contained none of the original betaine, formed a solid glassy mass on cooling. When this was ground up with ether, orange crystals were formed; these were filtered off and washed with ether. Yield 0.70 g. A further 0.15 g of this substance was isolated from the ethereal solution. The compound was crystallized 3 times from methanol. Orange crystals with m.p. 91.5-92.5°, soluble in acetone and benzene.

Found %: N 14.00, 14.26. $C_{16}H_{17}O_3N_3$. Calculated %: N 14.04.

The betaine isomerization product was identical with the compound formed by the acylation of N,N,N'-trimethyl-p-phenylenediamine [7] with p-nitrobenzoyl chloride.

The nitrobenzoyl group in the prepared anilide is fairly easily hydrolyzed and this is apparently the result of its solubility in acids and the influence of the ammonium group thus formed on the acylamino group. When a solution of 0.1 g of the substance in 5 ml hydrochloric acid (d 1.19) and 5 ml water was boiled (2 hours), a precipitate (0.05 g) was obtained which proved to be p-nitrobenzoic acid. The action of excess alkali on the filtrate led to the separation of N,N,N'-trimethyl-p-phenylenediamine, which was converted, by the action of p-toluenesulfonyl chloride in pyridine, to the N'-p-toluenesulfonyl derivative (yield 64 %), which proved to be identical with the product of methylation of p-toluenesulfamino-N,N-dimethylaniline (p-toluenesulfonamido-N,N-dimethylaniline) [7].

b) Preparation from N,N,N'-trimethyl-p-phenylenediamine. A solution in benzene of N,N,N'-trimethyl-p-phenylenediamine, prepared by the hydrolysis of p-toluenesulfonyl 4-dimethylamino-N-methylanilide (4'-dimethylamino-N-methyl-p-tolylsulfonanilide) [7], was mixed with a solution of p-nitrobenzoyl chloride in benzene; the precipitate obtained was separated and the benzene solution washed with hydrochloric acid. When the precipitate and the hydrochloric acid extracts were treated with ammonia, a tarry substance was formed which crystallized when ground up with ether. M. p. 91.5-92° (from methanol); a mixture of the substance with the product obtained as described in a) showed no melting point depression.

p-Toluenesulfonyl 4-dimethylamino-N-methylanilide. (4'-Dimethylamino-N-methyl-p-tolylsulfonanilide) The compound was prepared from p-toluenesulfamino-N,N-dimethylaniline (p-toluenesulfonamido-N,N-dimethylaniline) (m.p. 131-132° [8]) by methylating it (in the form of its sodium derivative) with methyl iodide [7], and also by Rodionov's method (yield 90 %) using trimethylphenylammonium hydroxide as alkylating agent, as has been described for p-toluenesulfaminoquinoline (p-toluenesulfonamidoquinoline) [9]. In addition to the form with m.p. 101-101.5° [7], the compound also forms a low-melting form with m.p. 93-94° (from methanol or ether).*

p-Nitrobenzoyl 4-thiomethyoxy-N-methylanilide. (4'-Thiomethoxy-N-methyl-p-nitrobenzanilide). The compound, obtained from the isomerization of dimethyl-[4-(p-nitrobenzoylamino)-phenyl]-sulfonium betaine [1], contained no trace of the imidol form (the O-alkyl derivative), since after its aqueous alcohol solution had been heated with hydrochloric acid, no primary aromatic amine could be detected in the solution by the diazo reaction. The anilide and the original betaine were fused with methyl p-toluenesulfonate at 140-150°, the same sulfonium salt being obtained in both cases, m.p. 180°.

4-(p-Nitrobenzenesulfamino)-N,N-dimethylaniline. (4-(p-Nitrobenzenesulfonamido)-N,N-dimethylaniline) The compound was prepared by the interaction of p-nitrobenzenesulfonyl chloride and p-aminodimethylaniline in pyridine solution. Orange crystals (from alcohol) with m.p. 189-190° (with decomp.), soluble in pyridine and benzene.

Found %: S 9.86, 9.94. $C_{14}H_{15}O_4N_3S$. Calculated %: S 9.98.

4-(p-Nitrobenzenesulfamino)-N,N-dimethylaniline 4-(p-Nitrobenzenesulfonamido)-N,N-dimethylaniline methyl-p-toluenesulfonate. Colorless crystals (from alcohol) with m.p. 201-203° (with decomp.).

Found %: S 12.57. $C_{22}H_{25}O_7N_3S_2$. Calculated %: S 12.63.

4-(p-Nitrobenzenesulfamino)-N,N-dimethylaniline (4-(p-Nitrobenzenesulfonamido)-N,N-dimethylaniline) methylbetaine (IIIa). A few drops of ammonia solution were added to a hot solution of 0.5 g of the original quaternary salt in 5 ml water until a faint odor was apparent. The yellow-orange crystals which precipitated on cooling were dried in a desiccator over caustic alkali. Yield 0.30 g (90 %). The compound is soluble in water, alcohol, acetone and pyridine, insoluble in benzene and dioxan. The melting point depends on the rate of heating and lies between 190 and 200°. The betaine reacts readily with dilute acetic acid and adds on 2 molecules of water when left to stand over 2 N alkali solution.

Found %: S 9.59. $C_{15}H_{17}O_4N_3S$. Calculated %: S 9.56.

p-Nitrobenzenesulfonyl 4-dimethylamino-N-methylanilide. (4-Dimethylamino-N-methyl-p-nitrobenzenesulfonanilide) a) From N,N,N'-trimethyl-p-phenylenediamine. 0.37 g p-nitrobenzenesulfonyl chloride was added to a solution of 0.25 g of the diamine in 4 ml pyridine and the mixture heated for 10 minutes at 80°; next day 30 ml water was added. The precipitate was crystallized from ethanol (yield 0.32 g), and then twice from methanol. Dark red crystals, soluble in benzene and ether, with m.p. 140-141°.

Found %: N 12.33, 12.41. $C_{15}H_{17}O_4N_3S$. Calculated %: N 12.53.

b) From 4-(p-Nitrobenzenesulfamino)-N,N-dimethylaniline (4-(p-nitrobenzenesulfonamido)-N,N-dimethylaniline) methylbetaine. 0.2 g of the betaine was placed in a test tube, which was then immersed in an oil bath heated to 200°, and heating continued for 10 minutes. The melt was cooled, ground up with ether, and the isomerization product extracted repeatedly with ether. The extract was washed with dilute alkali and dried with potassium carbonate. The residue left after distillation of the ether (0.05 g) was crystallized from methanol. The substance was identical with the product obtained as described in a).

SUMMARY

The following dipolar ions of the ammonium series have been prepared: 4-(p-nitrobenzoylamino)-N,N--dimethylamine methylbetaine and 4-(N-nitrobenzenesulfamino)-N,N-dimethylaniline (4-(N-nitrobenzenesulfonamido)-N,N-dimethylaniline) methylbetaine.

It has been established that when heated above their melting point these compounds undergo rearrangement with the formation of the N-alkylanilides: p-nitrobenzoyl 4-dimethylamino-N-methylanilide (4'-dimethylamino-

* The presence of two forms has also been established for toluenesulfonyl derivatives of certain halogenoanilines [10].

-N-methyl-p-nitrobenzanilide) and p-nitrobenzenesulfonyl 4-dimethylamino-N-methylanilide, (4'-dimethylamino-N-methyl-p-nitrobenzenesulfonanilide), respectively.

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• Original Russian pagination. See C. B. Translation.

THE SYNTHESIS AND FUNGISTATIC ACTIVITY OF CERTAIN PENTACHLOROPHENOL DERIVATIVES

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The very readily available product, pentachlorophenol, like other halogenophenols, exhibits a high fungistatic activity. Its high toxicity, however, prevents its application in medicine for the treatment of fungal infections.

The literature [1, 2] contains descriptions of attempts to prepare derivatives of halogenophenols possessing a sufficient fungistatic activity and comparatively low toxicity. In these works comparatively little attention has been paid to derivatives of pentachlorophenol.

In order to study the relationship between the fungistatic activity of these compounds and their chemical structure we have prepared a number of esters of pentachlorophenol and fatty acids, together with the benzoic and phenylacetic esters. We have also synthesized certain other derivatives of pentachlorophenol containing alcoholic groups (the α-pentachlorophenyl ethers of glycol and glycerol), the keto group (pentachlorophenoxyacetone and ω-pentachlorophenoxy-4-methoxyacetophenone) and the carboxyl group (methyl α-pentachlorophenoxybutyrate).

The synthesis of the pentachlorophenolic esters was achieved by the interaction of the chloride or anhydride of the acid in question with pentachlorophenol in pyridine; in this way it was established that pentachlorophenyl butyrate has m.p. 75-76° and not 59-62°, as described in the literature [3]. The remaining derivatives described by us were prepared by the reaction of the appropriate halogeno derivative with sodium pentachlorophenoxide.

The properties of the compounds prepared by us are given together with their bacterio- and fungistatic activity in the Table. The activity of the pentachlorophenol derivatives was determined in experiments in vitro and the Table shows the maximum dilution of the specimen at which complete suppression of microorganism development took place. The Table shows the bacterio- and fungistatic activity relative to acid-resistant bacteria and pathogenic fungi, since these organisms have proved to be most sensitive to pentachlorophenol derivatives. It has been established that all the derivatives which we have prepared are considerably less active than the original pentachlorophenol; the activity of the esters in the case of the monobasic fatty acids decreases with increase in the molecular weight of the acid. The slight increase in fungistatic activity in the case of pentachlorophenyl propionate when compared with the acetate is probably explained by the fact that the propionic acid, which may be formed by hydrolysis, does itself exhibit a noticeable activity. In agreement with the literature data [1], pentachlorophenoxyethanol exhibits appreciable fungistatic action. The activity of glycerol pentachlorophenyl ether is considerably lower. The remaining derivatives are of little interest.

EXPERIMENTAL

The pentachlorophenyl esters were prepared as follows: 0.010 mole pentachlorophenol, 0.011 mole of the acid chloride and 10 ml pyridine were heated on a boiling water bath for 1 hour. The mixture was then poured into dilute hydrochloric acid solution (1 : 10). The substance was extracted with ether. The ether extract was washed with water, then with sodium bicarbonate solution, again with water and finally dried with anhydrous sodium sulfate.

Specimen No.	Name	Melting point	Empirical Formula	% Cl		Bacterio- and fungistatic activity **					
				Found	Calculated	acid-resistant bacteria			pathogenic fungi		
						human tuberculosis bacillus	avian tuberculosis bacillus	acid-resistant saprophyte B5	Downy microsporum	trichophyton gypseum	achorion Schoenleinii
1	Pentachlorophenol	186-187°	C_6HOCl_5	–	–	1:256000	1:128000	1:64000	1:512000	1:256000	–
2	Petachlorophenyl acetate	151.5-152	$C_8H_5O_2Cl_5$	–	–	1:32000	1:16000	1:4000	1:4000	1:8000	1:16000
3	Pentachlorophenyl propionate	79-79.5	$C_9H_5O_2Cl_5$	–	–	1: 128000	1:16000	1:16000	1:64000	1:64000	1:256000
4	Pentachlorophenyl butyrate	75-76	$C_{10}H_7O_2Cl_5$	52.77	52.73	–	–	–	1:2000	1:1000	1:1000
5	Petachlorophenyl valerate	57	$C_{11}H_9O_2Cl_5$	50.91	50.61	1:32000	1:32000	1:8000	0	0	0
6	Pentachlorophenyl pivalate	105.5-106	$C_{11}H_9O_2Cl_5$	51.36	50.61	0	0	0	0	0	0
7	Pentachlorophenyl isovalerate	82-82.5	$C_{11}H_9O_2Cl_5$	50.98	50.61	1:1000	0	0	0	0	0
8	Pentachlorophenyl caproate	57-57.4	$C_{12}H_{11}O_2Cl_5$	48.49	48.67	1:32000	1:8000	1:1000	1:1000	1:2000	1:2000
9	Pentachlorophenyl oenanthate (n-heptylate)	47-47.2	$C_{13}H_{13}O_2Cl_5$	46.87	46.87	1:2000	1:2000	0	0	0	0
10	Pentachlorophenyl caprylate	49.7-50	$C_{14}H_{15}O_2Cl_5$	44.96	45.19	0	0	0	1:4000	1:4000	1:4000
11	Pentachlorophenyl pelargonate	57.5-57.7	$C_{15}H_{17}O_2Cl_5$	43.63	43.64	0	1:1000	0	0	1:1000	0
12	Pentachlorophenyl stearate	81.5	$C_{24}H_{35}O_2Cl_5$	33.3	33.3	0	0	0	0	0	0
13	Pentachlorophenyl benzoate	162.5-163.5	$C_{13}H_5O_2Cl_5$	–	–	–	–	–	0	0	0
14	Pentachlorophenyl phenylacetate	103-103.3	$C_{14}H_7O_2Cl_5$	46.22	46.14	1:32000	1:4000	0	1:4000	0	1:1000
15	β-Pentachlorophenoxyethanol	91-92	$C_8H_5O_2Cl_5$	–	–	1:8000	1:64000	1:4000	1:64000	1:64000	1:64000
16	Glycerol pentachlorophenyl ether	109.5-110.5	$C_9H_7O_3Cl_5$	52.36	51.1	1:64000	0	0	1:8000	1: 4000	1:16000
17	Pentachlorophenoxyacetone	106.5-106.7	$C_9H_5O_2Cl_5$	55.41	55.02	1:256000	1:32000	1:16000	0	0	0
18	Pentachlorophenoxyacetone thiosemicarbazone	125-125.5	$C_{10}H_8ON_3Cl_5S$	10.81*	10.86*	1:2000	1:2000	1:2000	1:8000	1:16000	1:8000
19	ω-Pentachlorophenoxy-4--methoxyacetophenone	148.5-149.5	$C_{15}H_9O_3Cl_5$	42.87	42.77	0	0	0	0	0	0
20	Methyl α-pentachlorophenoxybutyrate	69.5-70	$C_{11}H_9O_3Cl_5$	48.67	48.67	0	0	0	0	0	0
21	1,2-Dipentachlorophenoxyethane	223-223.3	$C_{14}H_4O_2Cl_{10}$	62.94	63.48	0	0	0	0	0	0

* Analysis data for nitrogen.

** The specimens were tested starting at a dilution of 1 : 1000.

The ether was distilled off and the substance recrystallized, generally from methanol (pentachlorophenyl stearate was recrystallized from ethyl acetate).

When the substance crystallized after the mixture had been poured into the hydrochloric acid, it was filtered off, washed with water, dried and recrystallized.

β-Pentachlorophenoxyethanol. 1 g caustic potash was dissolved in 10 ml butyl alcohol, 2.66 g pentachlorophenol was added and when this had dissolved 1.61 g of ethylene chlorohydrin was added. The mixture was boiled for 2.5 hours.

The butanol was distilled off in vacuo, the residue treated with 50 ml water, the precipitate filtered off and washed with water until the washings showed no alkaline reaction. The product was crystallized from alcohol. This yielded 0.6 g of substance with m.p. 91-92°; 0.2 g of substance with m.p. 86-87° was obtained from the mother liquor. Literature data: m.p. 92-94° [1].

Glycerol α-pentachlorophenyl ether. 0.15 g caustic soda was dissolved in 3.5 ml water, 1 g pentachlorophenol added, and when this had dissolved 0.42 g of glyceryl chlorohydrin was added. The mixture was heated on a boiling water bath for 1 hour. Phenolphthalein was used to test for completion of the reaction. When the mixture was cooled, crystals separated which were difficult to filter and these were extracted with ethyl acetate. The ethyl acetate extract was dried with anhydrous sodium sulfate, shaken up for 30 minutes with charcoal and filtered. The ethyl acetate was distilled off in vacuo at 45°. The residue was recrystallized once from dichloroethane, then 3 times from alcohol. M.p. 109-110.5°.

Pentachlorophenoxyacetone. A mixture of 2.66 g pentachlorophenol, 0.65 g (15% excess) caustic soda, 1 ml (15 % excess) chloroacetone and 10 ml alcohol was left for 4 hours at room temperature. It was then heated to the boil for 1 hour. The reaction mass was poured into water, to which 5 ml 10 % sodium carbonate solution had been added. The substance which precipitated was filtered off and recrystallized twice from methanol. This yielded 0.73 g of substance with m.p. 106.5-106.7°.

Pentachlorophenoxyacetone thiosemicarbazone. 0.75 g pentachlorophenoxyacetone was dissolved in alcohol and an aqueous solution of 0.75 g thiosemicarbazide hydrochloride added. The substance which precipitated was filtered off and recrystallized from alcohol. M.p. 125-125.5°.

ω-Pentachlorophenoxy-4-methoxyacetophenone. A mixture of 1.44 g pentachlorophenol, 0.33 g caustic potash, 5 ml ethyl alcohol and 1.15 g p-methoxyphenacyl bromide was heated on the water bath. After 5 minutes the contents of the flask had solidified to a thick crystalline mass to which 5 ml alcohol was added, and boiling continued for a further 30 minutes, after which the mixture was poured into 40 ml water. The precipitate obtained was dried at 60°. This yielded 2.18 g of substance with m.p. 148.5-149.5° (from alcohol).

Methyl α-pentachlorophenoxybutyrate. A mixture of 2.66 g pentachlorophenol, 0.62 g caustic potash, 2.26 g methyl α-bromobutyrate and 10 ml ethyl alcohol was boiled for 3 hours. 100 ml water and 5 ml 10 % caustic soda solution were poured into the mixture which was then extracted with ether. The ether was distilled off and the substance recrystallized from methyl alcohol. This yielded 1.55 g of substance with m.p. 69.5-70°.

1,2-Dipentachlorophenoxyethane. A mixture of 2 g pentachlorophenol, 0.22 ml ethylene dibromide, 0.42 g caustic potash and 5 ml alcohol was boiled for 4 hours. The mixture was then poured into 50 ml water, 2 ml alkali added and theprecipitate obtained filtered off, washed with alkali and then with water, and dried. M. p. 223-223.3° (from ethyl acetate).

SUMMARY

A number of pentachlorophenol derivatives have been synthesized and their bacterio- and fungistatic activity studied.

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ORIENTATION IN AROMATIC SUBSTITUTION

II. ELECTRONIC SHIFTS IN THE BENZENE NUCLEUS

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In the present communication an attempt is made to develop theories of electronic shifts in the aromatic nucleus which explain the phenomena observed during substitution reactions and the properties of the substituted compounds.

It is known that in a molecule there may take place a shift of the electron doublet of a covalent bond toward the more electronegative atom of group, this shift being known as the inductive effect. This effect is rapidly damped out when transmitted along a chain of atoms.

At the present time it is recognized that in molecules with conjugated bonds "there exists a specific mechanism by which the mutual influence between atoms is transmitted, this mechanism being different in character from that by which effects are transmitted along a chain of σ-bonds, and caused by the conjugation" [1]. The main difference lies in the fact that ". . . the influence is readily transmitted along a conjugated chain for comparatively great distances without significant damping off."

It seems to us that there are not sufficient grounds for considering it to be different in character from the inductive effect. The difference is here rather one of degree and arises from the fact that, as a result of the mobility of the π-electron clouds, the damping of the effect of their shift is not so rapid as in the case of the σ-bond clouds.

In the benzene nucleus under the influence of a substituent there will take place a shift of the electron clouds of both σ- and π-bonds. This shift will take place through the nucleus either towards the substituent or away from the substituent, depending on its nature, and will take place along both the right-hand and left-hand branches of the nucleus away from the substituent. For example, in monosubstituted benzene with a substituent of the 1st type (OH, CH_3, NH_2 etc.) the shift takes place away from the substituent so that the center of the electron cloud between atoms 1 and 2 is displaced from the mid-point by an amount a, the same as the displacement between atoms 1 and 6 (Fig. 1.). Under the influence of this shift a displacement of the center of the electron cloud takes place in the same direction between the atoms 2 and 3 by an amount b which is the same as that between the atoms 6 and 5. A further transmission of the shift takes place between atoms 3 and 4 by an amount c, the same as that between atoms 5 and 4. In this way the centers of the electron clouds approach the para-carbon atoms from two directions.

The magnitudes of the displacements of the electron cloud centers are related to one another in the following way

$$a > b > c. \qquad (I)$$

This inequality may be written down since the displacement is slightly damped with increase in the distance from the substituent. The second relationship

$$a - b > b - c \qquad (II)$$

shows that the magnitude of the damping effect a−b on going from the first to the second stage of the displacement is greater than the magnitude of the damping effect b − c on going from the second to the third stage of the displacement. Since the damping effect takes place by a definite fraction of the shift, this fraction of a

will be greater than that of b, while the fraction of b will be greater than that of c. The third realtionship

$$b > a - b \text{ and } c > b - c \qquad \text{(III)}$$

shows that the displacement of the electron cloud centers between the atoms is greater than the magnitude of the damping effect. If the damping effect were greater than the displacement following it, then after 2-3 atoms along the chain the effect would be greatly reduced, whereas it is well known that the effect is transmitted with little damping off along a conjugated system.

Let us now examine the distances between the electron cloud centers for different atoms in the nucleus and from this the electron density at each carbon atom. If we take the distances between the carbon atoms as equal to 1, then the distances between the electron cloud centers at each carbon atom of a nucleus with a substituent of type I will have the magnitudes given in Column 2 of Table 1, as follows from Fig. 1. By comparing the distances between the electron cloud centers, it is not difficult to show that at the third carbon atom this distance is greater than at the second and fourth, i.e. : $1 - b + c > 1 - a + b$ and $1 - b + c > 1 - 2c$ (by cancelling and changing the sign we obtain the expressions II and III). The density of the electron cloud at the atoms 2 and 4 is thus greater than at atom 3, and this means that in reactions with an electrophilic reagent the substitution will proceed for the most part in the ortho- and para-positions to the substituent.

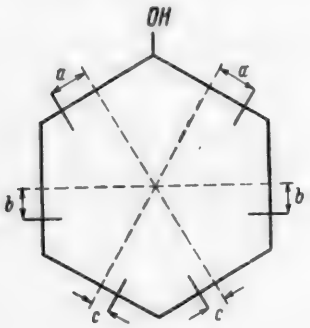

Fig. 1.

TABLE 1

The Distances Between the Electron Cloud Centers in Monosubstituted Derivatives of Benzene

Carbon atom No.	Distance between electron cloud centers with substituent	
	of type I	of type II
1	$1 + 2a$	$1 - 2a$
2	$1 - a + b$	$1 + a - b$
3	$1 - b + c$	$1 + b - c$
4	$1 - 2c$	$1 + 2c$
5	$1 - b + c$	$1 + b - c$
6	$1 - a + b$	$1 + a - b$

If there is present in the nucleus a substituent of type II (NO_2, SO_3H, COOH etc.), which repels electrons from the nucleus, then the displacement of the electron clouds will take place in the opposite direction, as shown in Fig. 2. The distances between the centers of the electron clouds for the carbon atoms of the nucleus are given in Column 3 of Table 1. From a comparison of the distances between the electron cloud centers it can easily be seen that this distance is less at the 3rd carbon atom than at the 2nd and 4th : $1 + b - c < 1 + a - b$ and $1 + b - c < 1 + 2c$, i.e. the density of the electron cloud at the 3rd atom is greater than at the 2nd and 4th, and in reactions with an electrophilic reagent, substitution will take place in the meta-position to the substituent.

The distances between the electron cloud centers at the atoms 2, 3, 4, 5 and 6 in a substituted benzene containing a substituent of type I are less than unity, as shown in Table 1, i.e. the density of the electron clouds is less than in the unsubstituted benzene, which leads to a deactivation of the nucleus towards electrophilic reagents.

It is well known that in the reactions of an electrophilic reagent with benzene containing a substituent of type I, the para-isomer is almost always formed predominantly. Cases in which the ortho-substituted compounds are formed are very rare, in spite of the fact that in the substituted benzene there are two ortho-positions and one para-position. The higher reactivity of the para-position towards electrophilic reagents is explained by the greater electron density at the para-position, since the distance between the electron cloud centers at atom 4 is less than at atom 2: $1 - 2c < 1 - a + b$.

Monosubstituted compounds with groups of type II are nitrated predominantly in the meta-position and to a considerable extent in the ortho-position, whereas the para-isomer is formed in very small quantities. With a group of type II the distance between the electron cloud centers at atom 2 is less than at atom 4: $1 + a - b < 1 + 2c$, and consequently the reactivity of the ortho-position is greater than that of the para-position.

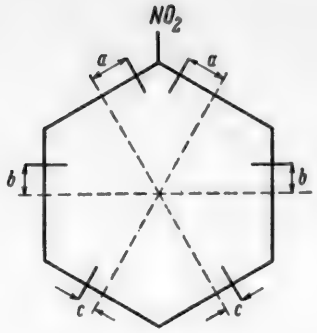

Fig. 2.

In a sulfonation reaction no significant quantities of the ortho-isomer are formed, as a result of the spatial factors which hinder the entry of the sulfonic acid group into the nucleus. Let us determine the relative distances between the electron cloud centers and consequently the electron densities at each carbon atom in a nucleus with two substituents, one of which, X, is attached to the 1st carbon atom and is electron-repelling (OH, NH_2, CH_3 etc.), while the other, Y, is electron attracting (NO_2, SO_3H, COOH etc.). The results of the determination for the ortho-isomer are given in Column 2 of Table 2. Thus the distance between the electron cloud centers at the 1st carbon atom is found in the following manner. The center of the cloud between atoms 1 and 6 in the unsubstituted benzene lies at a distance 0.5 from the 1st atom. The substituent X repels it by a distance a, while the substituent Y, by attracting the electron cloud, reduces this by an amount b. Between atoms 1 and 2 the center of the cloud, in the absence of substituents lies at a distance 0.5 from the 1st atom. The substituent X repels it by the distance a, while the substituent Y, by attracting it, increases the distance by a further amount a. By adding, the distance between the electron cloud centers at the 1st carbon atom is found to be equal to $0.5 + a - b + 0.5 + a + a = 1 + 3a - b$.

TABLE 2

The Distance Between the Electron Cloud Centers with a Susbtituent of Type I and a Substituent of Type II in the Nucleus

Carbon Atom No. in the nucleus	Distance between electron cloud centers		
	ortho-isomer	meta-isomer	para-isomer
1	$0.5 + a - b + 0.5 + a + a = 1 + 3a - b$	$1 + 2a + b - c$	$1 + 2a + 2c$
2	$0.5 - a - a + 0.5 - a + b = 1 - 3a + b$	1	$1 - a + 2b - c$
3	$0.5 - b + a + 0.5 + c - b = 1 + a - 2b + c$	$1 - 2a - b + c$	$1 + a - 2b + c$
4	$0.5 - c + b + 0.5 - c - c = 1 + b - 3c$	$1 + a - b - 2c$	$1 - 2a - 2c$
5	$0.5 + c + c + 0.5 - b + c = 1 - b + 3c$	1	$1 + a - 2b + c$
6	$0.5 - c + b + 0.5 - a + b = 1 - a + 2b - c$	$1 - a + b + 2c$	$1 - a + 2b - c$

Table 2 shows the calculated distances between the electron cloud centers at all six carbon atoms for all three isomers. Table 3 shows the distances, calculated in the same way, between the electron cloud centers at the carbon atoms in the nucleus when two substituents of type I or two substituents of type II are present. By comparing these distances it is possible to estimate the relative reactivity of disubstituted benzene in the introduction of

TABLE 3

The Distance Between the Electron Cloud Centers in Disubstitued Derivatives of Benzene

Carbon atom No. in the nucleus	Two substituents of type I; isomers:			Two substituents of type II; isomers:		
	ortho-	meta-	para-	ortho-	meta-	para-
1	$1 + a + b$	$1 + 2a - b + c$	$1 + 2a - 2c$	$1 - a - b$	$1 - 2a + b - c$	$1 - 2a + 2c$
2	$1 + a + b$	$1 - 2a + 2b$	$1 - a + c$	$1 - a - b$	$1 + 2a - 2b$	$1 + a - c$
3	$1 - a + c$	$1 + 2a - b + c$	$1 - a + c$	$1 + a - c$	$1 - 2a + b - c$	$1 + a - c$
4	$1 - b - c$	$1 - a + b - 2c$	$1 + 2a - 2c$	$1 + b + c$	$1 + a - b + 2c$	$1 - 2a + 2c$
5	$1 - b - c$	$1 - 2b + 2c$	$1 - a + c$	$1 + b + c$	$1 + 2b - 2c$	$1 + a - c$
6	$1 - a + c$	$1 - a + b - 2c$	$1 - a + c$	$1 + a - c$	$1 + a - b + 2c$	$1 + a - c$

a third substituent into the nucleus or in the replacement of one of the substituents by another, by reaction with either electrophilic or nucleophilic reagents. Table 4 shows the results of the comparison. Thus when a substituent of type I (in position 1) and a substituent of type II are present in the nucleus, the reactivity in the introduction of a third substituent using an electrophilic reagent is determined in the following manner. By comparing the distances between the electron cloud centers in each isomer we find the smallest distance, i.e. the carbon atom, without substituent, which has the greatest electron density. In the ortho-isomer the greatest density lies at atom 4, where the distance between the cloud centers $1 + b - 3c$ is smaller than any other distance, as can easily be determined from the data in Table 2. In the meta-isomer the greatest electron density lies at atom 4 and in the para-isomer at atom 2 (or 6).

Position 4 in ortho-		position 4 in meta-		position 2 in para-
$1 + b - 3c$	<	$1 + a - b - 2c$	<	$1 - a + 2b - c$

The correctness of these relationships shows that the ortho-isomer is most reactive and the para-isomer least. Martinsen's experiments [2] in a study of the kinetics of nitration of o-, m- and p-nitrochlorobenzenes gave the following values for the reaction rate constants at 25°: K_o 7.15; K_m 0.39; K_p 0.18, i.e. they are also in the order o > m > p.

In a similar fashion it is found that with two substituents of type I the reactivities of the isomers in the introduction of a third substituent as a result of reaction with an electrophilic reagent lie in the order m > o > p (Table 4). The sulfonation of the isomeric xylenes [3] gives the same order for the reactivities of the isomers.

With two substituents of type II the reactivity of the meta-isomer is greater than that of the ortho- and para-isomers. The nitration of m- and p-dinitrobenzenes [4], and the sulfonation of the three isomeric benzenedicarboxylic acids [5], also agree with this order or reactivities. In reactions with nucleophilic reagents the reverse order of reactivities of the isomers is obtained.

Column 3 of Table 4 shows the reactivity in the replacement of one substituent by another. In the reactions of an electrophilic reagent with a compound having substituents of types I and II, the substituent of type II may be replaced. Thus in the reaction of water with sulfonic acids the sulfonic acid group is split off. Comparison of the distances between the electron cloud centers (Table 2) shows that the density of the electron cloud at the carbon atom connected to a sulfonic acid group is always greater than at the carbon atom with a substituent of type I. The order of reactivities p > o > m shown in Table 4, however, is not confirmed by experiment.

The ortho-isomer has the greatest tendency to undergo hydrolysis, followed by the para- and finally by the meta-isomer [6]. This example of the increase in reactivity of the ortho-isomer compared with the calculated reactivity is not the only exception, since in a number of other cases the ortho-isomer shows an increase reactivity. This is caused by the positioning next to one another of substituents which are able to interact with one another with the formation of hydrogen bonds or in some other fashion. Spatial factors may also have an influence on the reactivity of the meta-isomer. When the volume of the substituents is sufficiently large, their complanarity with the benzene ring may be disturbed, as takes place for example in o-dichlorobenzene [7].

The decarboxylation of substituted carboxylic acids is a second example of a similar order of reactivities of the isomers o > p > m. The halogeno-substituted carboxylic acids [8] and the hydroxybenzoic acids [9] are decarboxylated in this order.

In the reactions of a nucleophilic reagent with a compound having substituents of types I and II, the substituent which is replaced is that of type I, since it is the one bound to a carbon atom having a lower electron density than at the substituent of type II (Table 2). For the replacement of the chlorine atom in nitrochlorobenzenes by a methoxy group using sodium methoxide, Holleman and De-Mooy [10] found the following reaction rate constants at 85 and 110° respectively: K_o 0.369 and 3.09, K_p 1.39 and 11. 45; the meta-isomer gave no nitroanisole under these conditions. These results are in complete agreement with the order given in Table 4.

The relative magnitude of the electron densities at the atoms linked to the phenolic hydroxyl groups in the nitrophenols, m > o > p, corresponds to the values of the dissociation constants of the isomeric nitrophenols. p-Nitrophenol has the largest dissociation constant, since the electron pair binding the proton to the oxygen is more powerfully attracted toward the nucleus where the density of the electron cloud is less. Thus at 25° K_p $9.6 \cdot 10^{-8}$, $K_o 7.5 \cdot 10^{-8}$, K_m $1.0 \cdot 10^{-8}$ [11].

TABLE 4

The Reactivity of Disubstituted Derivatives of Benzene (X – Substituent of Type I; Y – of Type II)

Type of distributed derivative	Reactivity in reaction with an electrophilic reagent	
	in introduction of a third substituent	in replacement of one of the substituents by another
C_6H_4XY *		The substituent of type II is replaced
	o position 4 $1 + b - 3c$ > m position 4 in $1 + a - b - 2c$ > p position 2 in $1 - a + 2b - c$	p position 4 in $1 - 2a - 2c$ > o position 2 in $1 - 3a + b$ > m position 3 in $1 - 2a - b + c$
		The substituent of type I is replaced by a nucleophilic reagent
		p > o position 1 in all three > m $1 + 2a + 2c$ > $1 + 3a - b$ > $1 + 2a + b - c$
$C_6H_4X_2$	m position 4 in $1 - a + b - 2c$ > o position 4 in $1 - b - c$ > p position 2 in $1 - a + c$	p position 4 in $1 + 2a - 2c$ > o position 2 in $1 + a + b$ > m position 3 in $1 + 2a - b + c$
$C_6H_4Y_2$	m position 5 in $1 + 2b - 2c$ > p position 2 in $1 + a - c$ = o position 3 in $1 + a - c$	m position 3 in $1 - 2a + b - c$ > o position 2 in $1 - a - b$ > p position 4 in $1 - 2a + 2c$

* X – in position 1 in the nucleus.

With two substituents of type I, replacement of one of them by another may take place. The reactivities lie in the order p > o > m for an electrophilic reagent and in the reverse order for a nucleophilic reagent (Table 4). A study of the kinetics of the reaction of sodium methoxide with the isomeric dichlorobenzenes gave the following rate constants: K_m 0.0506, K_o 0.0382 and K_p 0.0114 [10], i.e. in agreement with the data given in Table 4.

In the reactions of an electrophilic reagent with a compound having two substituents of type II, the reactivities follow the order m > o > p. In the hydrolysis of the isomeric benzenedisulfonic acids, and also of the sulfonated benzoic acids [5], we again observe the discrepancy noted above, namely the increased reactivity of the ortho-isomer. The reactivity thus follows the order o > m > p. The meta-isomer is the most stable of the sulfonic acids, with a substituent of type I, toward hydrolysis, but in the case of a substituent of type II the para-isomer is the most stable. This fact is fully explained in the terms of the theories of electronic shift which we have presented.

With two substituents of type II the order of reactivities toward nucleophilic reagents is p > o > m. The kinetic experiments of Steger [12] on the replacement of the nitro group in the dinitrobenzenes using sodium ethoxide and methoxide at 25, 35 and 45° showed that in all cases the reaction rate constant for the para-isomer was greater than that of the ortho-isomer. The nitro group in the meta-isomer is not replaced by an alkoxy group [13].

Chlorine and other halogens orientate further substituents into the ortho- and para-positions, but deactivate the nucleus, and this does not seem at first glance to agree with the theories presented. The halogens do not always deactivate the benzene nucleus, however. For example, the nitration of o-nitrochlorobenzene proceeds more rapidly than in the case of benzene [2]. There is very little difference in the rate constants for the sulfonation of chlorobenzene ($10.6 \cdot 10^{-6}$ at 40°) and for the sulfonation of benzene ($15.5 \cdot 10^{-6}$) [14]. Since in chlorobenzene any of the six hydrogens may be replaced, it may be considered that the para-position in chlorobenzene is rather activated than deactivated.

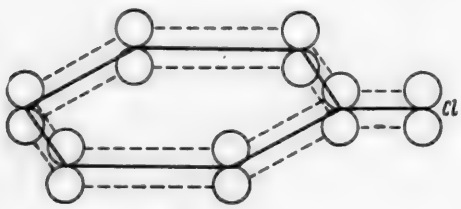

Fig. 3.

The deactivation of the nucleus by halogens is extremely weak. Thus whereas in the introduction of a second nitro group into the nucleus, the reaction rate constant is reduced by 10^5 - 10^7 times [15], in the entry of a 2nd chlorine atom the rate constant is reduced by only 8.5 times [16]. Naphthalenedisulfonic acid is sulfonated with a reaction rate several hundred thousand times less than that of the monosulfonic acid [17], but m- and p-chloronitrobenzenes are nitrated only 4 and 8 times slower than nitrobenzene [2].

The slight deactivation by a halogen is explained as follows. The halogen atom in the benzene nucleus has three pairs of unshared electrons. One of these pairs with a p function interacts with the π-electrons of the nucleus, forming a system of π-bonds, as shown in Fig. 3. Such a system of bonds is distinguished by increased stability by analogy with the stability and reduced reactivity of the benzyl radical compared with the phenyl and diphenyl radicals [18].

Chlorine and bromine are however considered to be more electronegative than the phenyl radical, so that it might be expected that an electronic shift toward the halogen would take place. This is so in the case where the unshared electron pairs of the halogen do not interact with other electrons, but in the halogeno-substituted benzene derivatives the halogen loses part of its electronegativity and the phenyl becomes more negative than the halogen.

The theories described cannot explain all the phenomena observed in substitution in the benzene nucleus or the properties of the substituted compounds, since the calculations are only of a qualitative and approximate character. Thus as a first approximation we have assumed that all substituents shift the electron cloud by identical amounts a, b and c. Spatial factors and other phenomena will also influence the magnitude of the shift. Our task is to find a reflection of these influences and arrive at a correct understanding of the true state of electron density distribution in the molecule.

SUMMARY

In the benzene nucleus, under the influence of a substituent, a displacement of the electron clouds takes

place through the nucleus away from the substituent or toward the substituent, depending on its nature, and this displacement takes place through both the left-hand and right-hand branches of the nucleus away from the substituent.

From this the relative density of the electron clouds at all the carbon atoms in the nucleus has been determined.

Reasons have been given for the orientation in the benzene nucleus containing substituents of types I and II, and for the activation and deactivation of the nucleus.

An explanation has been given for the order of the reactivities of the ortho-, meta- and para-isomers of disubstituted derivatives of benzene in the introduction of a third substituent and in the replacement of one substituent by another. An explanation has also been given for a number of other phenomena and properties of the substituted compounds.

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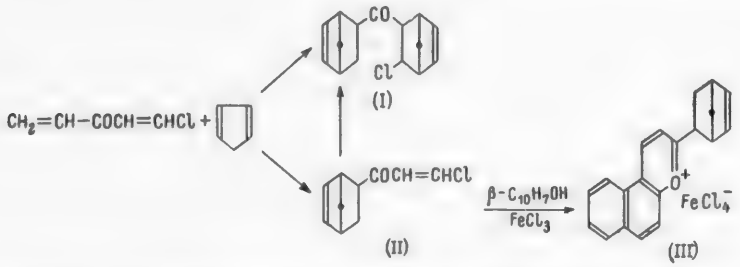
CONDENSATION OF ALKENYL β-CHLOROVINYL KETONES WITH CYCLOPENTADIENE

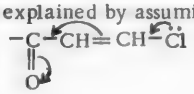
N. K. Kochetkov and B. P. Gottikh

Alkenyl β-chlorovinyl ketones RR'C=CHCOCH=CHCl, a method for whose synthesis was recently developed in our laboratory [1], have remained completely unstudied as regards their chemical behavior. Only on the example of reaction with β-naphthol [1] is the high reactivity of the chlorine atom contained in them known, a property that is common to all β-chlorovinyl ketones [2]. It seemed of considerable interest to determine the relative reactivity of the two double bonds found in alkenyl β-chlorovinyl ketones, and in particular, the dienophilic activity of this class of compounds. As is well known, α,β-unsaturated ketones are active dienophiles, in which connection the activity of a multiple bond depends on the character, number, and position of the substituents found on the carbon atoms bearing the multiple bond. In earlier studies made in our laboratory it was shown that the alkyl and aryl β-chlorovinyl ketones are also quite active dienophiles [3-5], in which connection the theory was expressed that the dienophilic activity of the β-chlorovinyl grouping is somewhat weaker than that shown by the vinyl group.

To determine the dienophilic activity of the β-chlorovinyl group relative to that shown by the vinyl and substituted vinyl groups we studied in the present paper the condensation of alkenyl β-chlorovinyl ketones, and specifically, of vinyl β-chlorovinyl ketone, propenyl β-chlorovinyl ketone and isobutenyl β-chlorovinyl ketone with cyclopentadiene. Depending on the relative activity of their double bonds, all of the enumerated alkenyl β-chlorovinyl ketones (RR'C=CHCOCH=CHCl) could give an adduct at either multiple bond, or a bis-adduct.

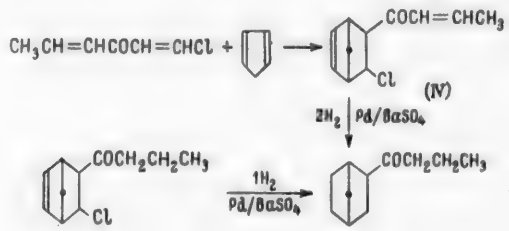
The condensation of vinyl β-chlorovinyl ketone with excess cyclopentadiene readily yields the bis-adduct (I). If the reaction is run with one mole of cyclopentadiene, then the mono-adduct—bicyclo(1,2,2)-hept-5-en-2--yl β-chlorovinyl ketone (II)—is formed. The structure of this compound is shown by the fact that when condensed with β-naphthol in the presence of ferric chloride it forms the corresponding 2-bicycloheptenylnaphthopyrylium ferrichloride (III). This reaction is characteristic for β-chlorovinyl ketones [6] and proves that the unchanged β--chlorovinyl grouping is present in the mono-adduct (II) obtained by us. Mono-adduct (II) readily condenses with a second molecule of cyclopentadiene and gives the bis-adduct (I), identical with that obtained by the direct reaction of vinyl β-chlorovinyl ketone with excess cyclopentadiene.



From the obtained results it follows that in vinyl β-chlorovinyl ketone the vinyl group actually possesses a higher dienophilic activity than does the β-chlorovinyl group, which is most easily explained by assuming that here the chlorine atom exerts a deactiviating influence in accord with the scheme  . We will

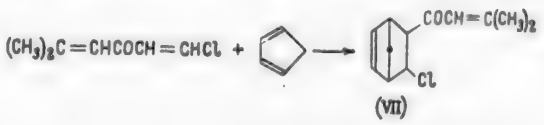
mention that this deactivating effect of substituents in the β-position of the vinyl group is expressed even more distinctly for the phenoxyvinyl ketones [7] and reaches its limit in the case of β-aminovinyl ketones, completely devoid of dienophilic activity [8].

The condensation of propenyl β-chlorovinyl ketone with cyclopentadiene yields the mono-adduct (IV). The structure of the obtained compound was shown by its hydrogenation over palladium-on-barium sulfate, where as the result of absorbing 2 moles of hydrogen the compound 2-butyryl-3-chlorobicyclo-(1,2,2)-heptane (V) was obtained, identical with the compound recently obtained by one of us and Khorlin [9] in the hydrogenation of 2-butyrylbicyclo-(1,2,2)-5-heptene.



The condensation of propenyl β-chlorovinyl ketone with excess cyclopentadiene under more drastic conditions with prolonged heating gave, together with the mono-adduct (IV), a certain amount of high-boiling substance, which in all probability, is the bis-adduct. That vinyl propenyl ketone shows a similar behavior was mentioned in one of the papers by I. N. Nazarov [10]. The experiments performed by us show that the β-chlorovinyl grouping possesses a higher dienophilic activity than does the propenyl grouping.

Finally, in the condensation of isobutenyl β-chlorovinyl ketone with cyclopentadiene this ketone also gives, even with an excess of the diene, only the mono-adduct (VII), the structure of which does not require proof since it is well known [10] that in diene synthesis reactions the isobutenyl group is considerably less active than the propenyl group, and consequently, also less active than the β-chlorovinyl group.



(VII)

It should be metnioned that in this case even the prolonged heating of isobutenyl β-chlorovinyl ketone with excess cyclopentadiene at 200° fails to give even traces of the bis-adduct, which again confirms the above cited data [10] regarding the passivity of isobutenyl ketones in diene synthesis reactions.

Summarizing the obtained results, it is possible to conclude that in their dienophilic activity the β-chlorovinyl ketones occupy a middle position between the vinyl ketones, on the one hand, and the propenyl ketones, on the other, and consequently the activity of the indicated type of α,β-unsaturated ketones can be expressed by the order:

$CH_2 = CHCOR > ClCH = CHCOR > CH_3CH = CHCOR > (CH_3)_2 = CHCOR.$

It should be added that our studied condensation of alkenyl β-chlorovinyl ketones with cyclopentadiene could also prove to be of preparative interest, since, utilizing the transformations studied in our laboratory of preparing 2-acyl-3-chlorobicycloheptanes [9, 11, 12] from adducts of alkenyl β-chlorovinyl ketones with cyclopentadiene, it becomes possible in case of need to obtain a number of alicyclic compounds that had not been available earlier.

EXPERIMENTAL

Bicyclo-[1,2,2]-hept-5-en-2-yl β-Chlorovinyl Ketone (II). To 17 g of vinyl β-chlorovinyl ketone with strong cooling was added in drops 9.5 g of freshly distilled cyclopentadiene. At the end of addition the mixture was allowed to stand for 10-12 hours at room temperature, after which the deposited crystals were filtered. Yield 13.2 g (50.3 %). After recrystallization from petroleum ether the substance melted at 44°, and had b.p. 102-103° (11 mm).

Found %: C 65.22, 65.20; H 6.18, 6.27. $C_{10}H_{11}OCl$. Calculated %: C 65.75; H 6.07.

Fine colorless crystals with characteristic odor, readily soluble in organic solvents, and insoluble in water; on storage the crystals gradually darken, but they can be kept for a long time in ether solution if hydroquinone is added.

3-Chlorobicyclo-[1.2.2]-hept-5-en-2-yl. Bicyclo-(1,2,2)-hept-5-en-2-yl Ketone (I). A. To 6.4 g of vinyl β-chlorovinyl ketone with strong cooling was added 10.7 g of freshly distilled cyclopentadiene; then the mixture was heated to the boil for 1 hour on the water bath. Vacuum-distillation gave 10 g of substance with b.p. 162-163° (8 mm), which crystallized completely. Yield 74 %. After a second distillation and recrystallization from petroleum ether the substance had m.p. 89-90° and b.p. 144.5-145° (4 mm).

B. To 3.1 g of mono-adduct (I) was added 2.4 g of freshly distilled cyclopentadiene and the reaction mixture was heated for 1 hour on the water bath. Two distillations in vacuo gave 3 g (70 %) of substance with m.p. 89-90° and b.p. 144-146° (4 mm). The mixed melting point with the substance, obtained by method A, was not depressed.

Found %: C 72.78, 72.55; H 7.01, 7.18. $C_{15}H_{17}OCl$. Calculated %: C 72.46; H 6.89.

Fine colorless crystals, readily soluble in organic solvents; can be stored for a long time without change.

2-(Bicyclo-[1.2.2]-hept-5-en-2-yl)-naphtho-(1,2;5',6')-pyrylium Ferrichloride (III). To solution of 1.8 g of mono-adduct (II) and 2 g of β-naphthol in 20 ml of glacial acetic acid was added a solution of 8 g of anhydrous ferric chloride in 12 ml of concentrated hydrochloric acid. The precipitate that deposited after several hours was filtered, washed with a small amount of glacial acetic acid, and then with absolute ether. The substance was obtained as dark-green crystals with m.p. 105-107°, insoluble in nonpolar solvents, rapidly decomposed with weak alkali solutions, suffering rapid tarring when stored, and not lending itself to purification.

3-Chlorobicyclo-[1.2.2]-hept-5-en-2-yl Propenyl Ketone (IV). To 19.5 g of propenyl β-chlorovinyl ketone was added 9.8 g of freshly distilled cyclopentadiene, the mixture allowed to stand for 10-12 hours at room temperature, and then heated for 0.5-1 hour on the water bath. Two distillations in vacuo gave 11.8 g (40.5 %) of substance with b.p. 107-109° (5 mm), n_D^{20} 1.5215, d_4^{20} 1.1456.

Found %: Cl 17.88. $C_{11}H_{13}OCl$. Calculated %: Cl 18.03.

Colorless oily liquid with characteristic camphor odor, miscible with organic solvents, gradually darkens on storage, and decomposes with the evolution of hydrogen chloride.

Hydrogenation of 3-Chlorobicyclo-[1.2.2]-hept-5-en-2-yl Propenyl Ketone. A solution of 5.8 g of adduct (IV) in 70 ml of absolute ether was hydrogenated at room temperature in the presence of 0.5 g of palladinized barium sulfate (palladium content 2 %). After 1040 ml of hydrogen (theory 1470 ml) had been absorbed the hydrogenation was stopped, since at this point hydrogen chloride began to form, testifying to the start of hydrogenolysis of the chlorine atom. After the usual workup and 2 vacuum-distillations we obtained 3.5 g (60 %) of 2-butyryl-3-chlorobicyclo-[1.2.2]-heptane (V).

B. p. 108-110° (5 mm), n_D^{20} 1.4855, d_4^{20} 1.0817, MR_D 53.55. Calc. 53.48.

Found %: Cl 17.22. $C_{11}H_{17}OCl$. Calculated %: Cl 17.66.

Literature data for 2-butyryl-3-chlorobicyclo-[1.2.2]-heptane: b.p. 108-110° (5 mm), n_D^{20} 1.4860, d_4^{20} 1.0781 [9].

Colorless liquid, miscible with organic solvents, and gradually decomposing on storage with the evolution of hydrogen chloride.

3-Chlorobicyclo-[1.2.2]-hept-5-en-2-yl Isobutenyl Ketone (VII). To 5.7 g of isobutenyl β-chlorovinyl ketone was added 7.8 g of freshly distilled cyclopentadiene and the mixture was heated for 1 hour on the water bath. Two distillations in vacuo gave 6.2 g (75 %) of substance.

B. p. 104-104.5° (5 mm), n_D^{20} 1.5223, d_4^{20} 1.1103, MR_D 57.88; Calc. 57.16.

Found %: C 68.21, 68.45; H 7.30, 7.33. $C_{12}H_{15}OCl$. Calculated %: C 68.40; H 7.17.

Colorless liquid, miscible with organic solvents, and gradually decomposing on storage with the evolution of hydrogen chloride.

SUMMARY

1. The condensation of alkenyl β-chlorovinyl ketones with cyclopentadiene, proceeding by the diene synthesis scheme, was studied.

2. It was shown that in their dienophilic activity the β-chlorovinyl ketones occupy an intermediate position between the vinyl ketones and the propenyl ketones. The dienophilic activity of the α,β-unsaturated ketones decreases in the order

$CH_2 = CHCOR > ClCH = CHCOR > CH_3CH = CHCOR > (CH_3)_2C = CHCOR$.

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SOME DERIVATIVES OF 4,4'-DIHYDRAZINODIPHENYL SULFONE AND 4-HYDRAZINOPHENYL 2-ACETAMINO-5-THIAZOLYL SULFONE

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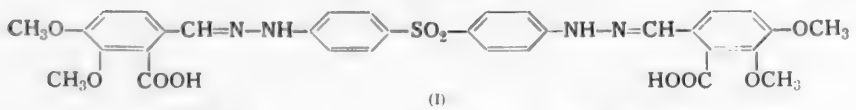
The problem of the present study was to synthesize some new derivatives of 4,4'-dihydrazinodiphenyl sulfone and 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone for the purpose of studying their antibacterial activity. A method for the preparation of 4,4'-dihydrazinodiphenyl sulfone has been sufficiently well developed by Sah [1]. The hydrazones of 4,4'-dihydrazinodiphenyl sulfone are easily obtained by the short heating of the dihydrochloride of 4,4'-dihydrazinodiphenyl sulfone with a slight excess of aromatic aldehydes (Table 1).

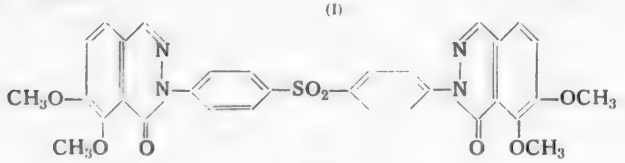
Depending on the conditions, the condensation of the dihydrochloride of 4,4'-dihydrazinodiphenyl sulfone with 3,4-dimethoxy-2-carboxy-benzaldehyde (opianic acid) yields two different substances. When the reaction is run in water or in sodium bicarbonate solution, with subsequent isolation of the substance by the addition of hydrochloric acid, a slightly colored compound (I) with m.p. 258-260° is obtained, readily soluble in sodium bicarbonate solution. Based on its elementary analysis this substance corresponds to the dihydrazone.

When the reaction is run in alcohol or aqueous alcohol a white substance (II) with m.p. 267-268° is obtained, insoluble in sodium bicarbonate solution. Substance (II) is easily obtained by boiling substance (I) in alcohol, but the reverse transformation could not be accomplished. Substance (II), insoluble in sodium bicarbonate, does not change when boiled for a long time with dilute acids or alkalies, or when heated with hydrazine hydrate, which indicates that the ester grouping is absent in it. Elementary analysis reveals that this compound contains two molecules of water less than does 4,4'-di-(3,4-dimethoxy-2-carboxybenzalhydrazino)diphenyl sulfone. Consequently, it can be assumed that compound (II) is a dehydration product of (I), the dehydration proceeding with the formation of two phthalazone nuclei similar to the formation of opiazone [2].

Our postulations were supported by means of infrared spectra, taken by Yu. N. Sheinker in the Physical Laboratory of the VNIKhFI.* The infrared spectrum of compound (II) shows an intense absorption band at 1667 cm^{-1}. As was shown earlier[3], this band corresponds to the carbonyl group in compounds containing the grouping $=N-\underset{|}{C}=O$, and in particular, is observed in phthalazones. As was to be expected, this band is absent in the spectrum of compound (I), which in structure is a normal dihydrazone. A band at 3280 cm^{-1}, observed in the spectrum of this compound, apparently corresponds to —NH— bonds. The absence of a well defined band for the OH group and of a band for carboxyl > C=O permits concluding that compound (I) exists as an internal salt, which is in excellent agreement with the ability shown by this compound to easily cleave water, with transformation into compound (II).



(I)



(II)

* All-Union Scientific-Research Chemical-Pharmaceutical Institute.

TABLE 1

Hydrazines	Aldehydes	Solvent	Yield of hydrazone (in %)	Melting point of hydrazone	Formula of hydrazone	Found (in %)			Calculated (in %)		
						C	H	N	C	H	N
4,4'-Dihydrazinodiphenyl sulfone dihydrochloride	4-Hydroxybenzaldehyde	water-alcohol (1:2)	60.7	238—240°	$C_{26}H_{22}O_4N_4S \cdot H_2O$	61.85	4.84	11.02	61.90	4.79	11.19
	4-Acetamidobenzaldehyde		61.7	262—265	$C_{30}H_{28}O_4N_6S \cdot H_2O$	61.99	4.95	14.37	61.41	5.15	14.32
	3-Methoxy-4-hydroxybenzaldehyde		54.5	250—252	$C_{28}H_{26}O_6N_4S$	61.54	4.83	10.09	61.52	4.79	10.25
	3,4-Dimethoxy-2-carboxybenzaldehyde	water	—	258—260	$C_{32}H_{30}O_{10}N_4S$	57.69	4.63	—	58.02	4.53	—
4-Hydroazinophenyl 2-acetamido-5-thiazolyl sulfone	4-Acetamidobenzaldehyde	water —10% CH_3COOH (1:3)	—	221—223	$C_{30}H_{10}O_4N_5S_2 \cdot H_2O$	50.76	4.45	—	50.50	4.43	—
	3-Methoxy-4-hydroxybenzaldehyde		—	238—240	$C_{19}H_{18}O_5N_4S_2$	51.16	4.23	12.55	51.11	4.06	12.57
	3,4-Dimethoxy-2-carboxylbenzaldehyde	water	—	263—264	$C_{21}H_{20}O_7N_4S_2$	50.37	4.89	—	49.96	4.99	—

Mono- and di-hydrazine analogs of "Promizole", i.e. of 4-aminophenyl 2-amino-5--thiazolyl sulfone, are not described in the literature. 4-Nitrophenyl 2-amino-5-thiazolyl sulfone was prepared by the method described in the literature [4], while the reduction of the nitro group was effected catalytically. Attempts to obtain 4-hydrazinophenyl 2-hydrazino-5--thiazolyl sulfone by the diazotization of promizole, followed by reduction of the diazo group, proved unseccessful, since here strong tarring occurred. It should be mentioned that for unsubstituted 2-aminothiazole the conversion into 2-hydrazino-thiazole by diazotization of the amino group, followed by reduction, could also not be accomplished [5]. The preparation of 4-hydrazinophenyl 2-acetamido--5-thiazolyl sulfone was more successfully accomplished by starting with 4-nitrophenyl 2-acetamido-5-thiazolyl sulfone, which was catalytically reduced to 4-aminophenyl 2--acetamido-5-thiazolyl sulfone. Diazotization of this sulfone, followed by reduction of the diazo derivative with stannous chloride, gave the hydrochloride of 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone and the free base. The condensation of 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone with aromatic aldehydes in water solution or in 10% acetic acid gave the corresponding hydrazones (Table 1). All of the obtained compounds were tested in the Chemotherapy Division of VNIKhFI under the direction of G. N. Pershina for their action of various microorganisms (spectrum of 16 species). The bacteriostatic activity of a number of the compounds toward tuberculosis bacilli and pathogenic fungi is given in Table 2. The remaining compounds are completely inactive toward all of the species of bacteria examined.

EXPERIMENTAL

Condensation of 4,4'-dihydrazinodiphenyl Sulfone With 3,4-Dimethoxy-2-carboxybenzaldehyde. To a hot solution of 1.4 g of opianic acid in 50 ml of alcohol was added a hot solution of 1 g of 4,4'-dihydrazino-diphenyl sulfone dihydrochloride in 10 ml of water. The white precipitate that separated on boiling was filtered, washed with hot water, then with alcohol, and dried. We obtained 2.2 g of substance with m.p. 268-269°, insoluble in sodium bicarbonate solution, and remaining

unchanged when boiled for a long time with 10 and 20 % sodium hydroxide, hydrochloric acid and hydrazine hydrate.

Found %: C 61.02; H 4.10; N 8.82. Compound (II) $C_{32}H_{26}O_8N_4S$. Calculated %: C 61.32; H 4.18; N 8.94.

TABLE 2*

Name of compound	Activity in the dilutions						
	bacillus		acid-resistant saprophyte	Microsporon	Trichophyton	Achorion	Actinomycetales
	human tuberculosis	avian tuberculosis					
4,4-Dihydrazinodiphenyl sulfone dihydrochloride	1 : 32000	1 : 16000	1 : 128000	1 : 2000	1 : 1000	1 : 2000	1 : 2000
4,4'-Di-(p- hydroxybenzalhydrazino)diphenyl sulfone	1 : 8000	1 : 4000	1 : 4000	–	–	–	–
4-Hydrazinophenyl 2-acetamido--5-thiazolyl sulfone	1 : 1000	1 : 1000	1 : 1000	–	–	–	–

* The testing was done by S. N. Milovanova.

To a hot solution of 1,4 g of opianic acid in 110 ml of water was added with vigorous stirring a hot solution of 1 g of 4,4'-dihydrazinodiphenyl sulfone in 10 ml of water. The obtained light-yellow precipitate was filtered, washed well with hot water, then with alcohol, and dried. We obtained 2 g of substance, readily soluble in sodium bicarbonate solution, and with m.p. 258-260°.

Found %: C 57.69; H 4.63. Compound (I) $C_{32}H_{30}O_{10}N_4S$. Calculated %: C 58.02; H 4.53.

This substance when boiled with alcohol or with an alcohol solution of sulfuric acid was converted into a substance with m.p. 268-269°, insoluble in sodium bicarbonate solution, and not depressing the melting point when mixed with substance (II).

4-Aminophenyl 2-Amino-5-thiazolyl Sulfone. A mixture of 8 g of 4-nitrophenyl 2-amino-5-thiazolyl sulfone, 8 g of Raney nickel catalyst and 65 ml of ethyl alcohol was hydrogenated at atmospheric pressure and room temperature. At the end of hydrogenation the reaction mass was brought to the boil, the nickel filtered, the solution evaporated to dryness, and the residue recrystallized from anhydrous alcohol. Yield 6.23 g (87 %); m.p. 217--219° [4].

4-Aminophenyl 2-Acetamido-5-thiazolyl Sulfone. A suspension of 2 g of 4-nitrophenyl 2-acetamido-5--thiazolyl sulfone, 2.5 g of Raney nickel catalyst and 40 ml of water was hydrogenated at atmospheric pressure and room temperature. Then 10 % NaOH solution was added to the mixture to dissolve the precipitate, the nickel filtered from the solution, and the filtrate treated with 10 % hydrochloric acid to give a white crystalline precipitate, insoluble in water and organic solvents, and readily soluble in dilute alkali. Yield 1.24 g (69 %); m. p. 268-269° (agrees with the literature data [4]).

4-Hydrazinophenyl 2-Acetamido-5-thiazolyl Sulfone. A mixture of 5.4 g of 4-aminophenyl 2-acetamido--5-thiazolyl sulfone, 42 ml of glacial acetic acid, 21 ml of hydrochloric acid (d 1.2) and 10.5 ml of water was heated to obtain solution, then filtered, and cooled. To it at -1 to -5° with vigorous stirring was added a solution of 1.1 g of sodium nitrite in 5.3 ml of water. After standing for 30 minutes the solution of diazo compound was added at from 0 to -2° to a solution of 7.85 g of stannous chloride in 38.5 ml of hydrochloric acid (d 1.2), the mixture allowed to stand for 2 hours at 0°, and then kept at room temperature for 2 days. The obtained white precipitate was filtered, washed with alcohol, and dried. We obtained 0.55 g of substance. Recrystallization from 10 % HCl gave 0.3 g of 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone hydrochloride with m.p. 222°.

Found %: C 38.23; H 3.83; N 16.04. $C_{11}H_{13}N_4O_3S_2$. Calculated %: C 37.87; H 3.76; N 16.06.

After removal of the 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone hydrochloride the filtrate was

poured into 2.25 liters of water and treated with hydrogen sulfide. The precipitate of stannous sulfide was filtered, the filtrate evaporated to dryness, the residue dissolved in 10 ml of water, and its treatment with 25 % aqueous ammonia gave 1.6 g of 4-hydrazinophenyl 2-acetamido-5-thiazolyl sulfone as a white precipitate. Repeated recrystallization gave the free base with m.p. 243-245°, which when treated with 10 % hydrochloric acid gave the same hydrochloride with m.p. 221°.

SUMMARY

1. A method was developed for the catalytic reduction of 4-nitrophenyl 2-acetamido-5-thiazolyl sulfone and 4-nitrophenyl 2-amino-5-thiazolyl sulfone.

2. 4-Hydrazinophenyl 2-acetamido-5-thiazolyl sulfone and its condensation products with aromatic aldehydes were obtained.

3. The hydrazones of 4,4'-dihydrazinodiphenyl sulfone with various aromatic aldehydes were obtained.

4. Depending on the conditions, it was established that the condensation of 4,4'-dihydrazinodiphenyl sulfone with opianic acid yields two substances, one of which is the normal dihydrazone, while the other is a phthalazone derivative.

5. The obtained compounds are devoid of antibacterial activity, except for three substances, which show a slight activity toward tuberculosis bacilli.

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CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXVIII. SYNTHESIS OF HYDROXY AND DIMETHYLAMINO DERIVATIVES OF 2-PHENYLQUINOLINE

N. S. Kozlov and L. Yu. Pinegina

In this paper we present experimental material that is a continuation and further expansion of our earlier published studies [1, 2].

I. Joint Catalytic Condensation of Primary Aromatic Amines and Acetylene with Aromatic Hydroxyaldehydes. As had been established earlier [3], the indicated reaction can be used to synthesize hydroxy derivatives of α-phenylquinoline; by reacting 2-hydroxy-3-methylbenzaldehyde and 6-hydroxy-3-methylbenzaldehyde with aromatic amines and acetylene we synthesized the following compounds: 2-(2'-hydroxy-3'-methylphenyl)-6-methylquinoline (I), 2-(2'-hydroxy-3'-methylphenyl)-7-methylquinoline (II), 2-(6'-hydroxy-3'-methylphenyl)-quinoline (III), 2-(6'-hydroxy-3'-methylphenyl)-6-methylquinoline (IV), 2-(6'-hydroxy-3'-methylphenyl)-7-methylquinoline (V) and 2-(6'-hydroxy-3'-methyl-phenyl)-6,8-dimethylquinoline (VI).

All of these compounds are new.

II. Joint Condensation of Aromatic Amines and Acetylene With p-Dimethylaminobenzaldehyde. This reaction was studied for the first time in the present paper. Its use permitted us to synthesize the following dimethylamino derivatives of quinoline: 2-(4'-dimethylaminophenyl)-6-methylquinoline (VII), 2-(4'-dimethylaminophenyl)-6-methylquinoline (VIII) and 2-(4'-dimethylaminophenyl)-7-methylquinoline (IX).

Of the enumerated compounds only (VII) is mentioned in the literature [4], in which connection its constants are not given, while the other two compounds were first synthesized by us.

EXPERIMENTAL

The method used to run the syntheses and isolate the reaction products was similar to that already described by us earlier [3].

All of the synthesized hydroxy derivatives of 2-phenylquinoline show amphoteric properties – they possess well-defined basic properties and very weak acidic properties. In accord with this they are readily soluble in acids, in which connection the salts of these compounds remain in solution. When heated these compounds are also somewhat soluble in alkali solutions, imparting a yellow color to the solutions.

As the result of the joint condensation of p-dimethylaminobenzaldehyde with acetylene and the amines – aniline, m-toluidine and p-toluidine – we obtained crystalline reaction products, having comparatively high melting points. These products are readily soluble in acids, forming bright-red solutions. The color disappears when the acid solution is treated with alkali and a precipitate is formed. The point at which the color changes is very sharply defined, for which reason the indicated quinoline bases can be used as indicators. We were unable to isolate cyrstallline platinates when the synthesized quinoline bases were treated with chloroplatinic acid. The properties of the obtained compounds and the analysis data are presented in Table 1; the conditions used to run the syntheses are given in Table 2.

SUMMARY

1. The catalytic condensation of aromatic hydroxyaldehydes and a number of aromatic amines with acetylene

TABLE 1

Properties of Obtained Derivatives of 2-Phenylquinoline and Their Analysis Data

Compound Nos.	Yield (in %)	Properties			Analysis of the compounds							Analysis of platinates		
		external appearance	temperature		found %			Empirical formula	calculated %			found Pt(%)	Empirical Formula of platinate	calculated Pt (%)
			m.p.	m.p. of picrate	C	H	N		C	H	N			
(I)	30.5	Light-yellow crystals	169—170°	162—163°	—	—	5.76, 5.68	$C_{17}H_{15}ON$	—	—	5.62	21.64, 21.64	$C_{34}H_{32}O_2N_2Cl_6Pt$	21.55
(II)	43.5	Yellow crystals	102—103	203	82.23	6.22	5.75, 5.72	$C_{17}H_{15}ON$	81.93	6.02	5.62	21.27	$C_{34}H_{32}O_2N_2Cl_6Pt$	21.55
(III)	41.6	Yellow needle crystals	144—145	211—212	81.82	5.79	5.97, 5.98	$C_{16}H_{13}ON$	81.70	5.53	5.96	21.84	$C_{32}H_{28}O_2N_2Cl_6Pt$	22.24
(IV)	32.5	Yellow crystals	143	210—211	82.24, 82.14	6.04, 6.04	5.49, 5.65	$C_{17}H_{15}ON$	81.93	6.02	5.62	21.24	$C_{34}H_{32}O_2N_2Cl_6Pt$	21.55
(V)	43.4	Yellow crystals	174—175	231—232	82.15	6.05	5.41, 5.77	$C_{17}H_{15}ON$	81.93	6.02	5.62	21.72, 21.90	$C_{34}H_{32}O_2N_2Cl_6Pt$	21.55
(VI)	29.5	Yellow crystals	140—141	209—210	—	—	5.41, 5.53	$C_{18}H_{17}ON$	—	—	5.32	20.87	$C_{36}H_{36}O_2N_2Cl_6Pt$	20.90
(VII)	31.4	Greenish needle crystals	172	210—212	82.14, 82.24	6.32, 6.30	11.37, 11.11	$C_{17}H_{16}N_2$	82.26	6.45	11.29			
(VIII)	17.2	Yellow crystals	184—186	178—179	82.65, 82.50	7.19, 6.73	10.54, 10.46	$C_{18}H_{18}N_2$	82.44	6.87	10.69			
(IX)	12.6	Tiny reddish transparent prisms	175—176	Decomp. around 230°	—	—	10.74, 10.69	$C_{18}H_{18}N_2$	—	—	10.69			

TABLE 2

Conditions for the Preparation of 2-Phenylquinoline Derivatives

Compound Nos.	Starting substances				Time of saturating with acetylene (in hrs)	Total weight of crude product (in g)	Distillation					
	aldehyde* (g)	amine (g)	ethyl alcohol (ml)	mercuric chloride (g)			amount of distilled substance (g)	1st fraction		2nd fraction**		residue (in g)
								boiling point (pressure in mm)	weight (in g)	residue (in g)	weight (in g)	
(I)	A,4	p-Toluidine, 5	80	2	15	10.6	10	120—230° (3)	3.4	230—250° (3)	2.8	3.6
(II)	A,4	m-Toluidine, 5	40	2	15	9.75	9.7	95—160 (5)	2.8	160—190 (5)	3.9	2.9
(III)	B,5	Aniline, 6	60	5	19	14.0	13.7	105—190 (3)	4.4	190—230 (3)	4.3	4.3
(IV)	B,7	p-toluidine, 8.3	60	5	17	11.9	10	130—200 (2)	2.9	200—230 (2)	4.5	2.5
(V)	B,7	m-Toluidine, 8.3	60	5	17	15.1	6.8	130—210 (1)	1.7	210—240 (1)	3.2	1.8
(VI)	B,5	m-Xylidine,6.5	50	2	17	9.2	5	110—200 (2)	1.25	200—230 (2)	2.0	1.7
(VII)	C,11	Aniline,10	60	5	18	17.1	5.8	130—250 (2)	1.3	250—285 (2)	2.5	2.0
(VIII)	C,9	m-Toluidine, 10	50	5	18	11.7	6	140—250 (1)	1.6	250—290 (1)	2.1	2.2
(IX)	C,9	p-Toluidine, 10	60	5	17	17.3	5.2	150—230 (1)	1.5	230—280	1.4	2.1

* A — 2-hydroxy-3-methylbenzaldehyde, B — 6-hydroxy-3-methylbenzaldehyde, C — p-dimethylaminobenzaldehyde.

** The condensation product was isolated from the 2nd fraction.

was studied. Six new hydroxy derivatives of 2-phenylquinoline with the hydroxy group in the phenyl radical were synthesized.

2. The catalytic condensation of a number of aromatic amines and acetylene with p-dimethylaminobenzaldehyde was studied. Three dimethylamino derivatives of p-dimethylaminobenzaldehyde were synthesized, of which two are not described in the chemical literature.

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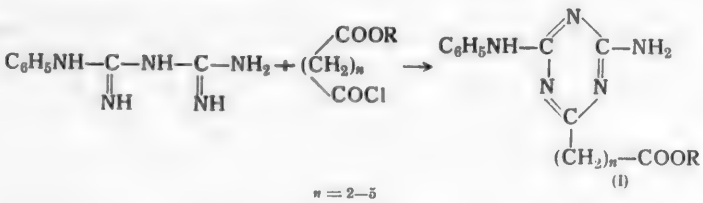
DERIVATIVES OF ω-(2,4-DIAMINO-1,3,5-TRIAZIN-6-YL)-ALKYLCARBOXYLIC ACIDS

IV. DERIVATIVES OF PROPIONIC, BUTYRIC, VALERIC AND CAPROIC ACIDS

S. V. Sokolovskaya, V. N. Sokolova and O. Yu. Magidson

Earlier [1, 2] we had studied the properties of the first two members of the ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkylcarboxylic acid series. It seemed of interest to extend this homologous series of acids and study the change in the properties of its members as a function of the length of the alkyl chain.

Thurston [3, 4] obtained some 2,4-diamino-1,3,5-triazin-6-yl-alkylcarboxylic acids by reacting biguanide with the diesters of dibasic carboxylic acids. In the present study the authors used the earlier proposed [5] method, which permitted obtaining 2,4-diamino-1,3,5-triazin-6-ylalkylcarboxylic acids in good yields. β-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic, -γ-butyric, -δ-valeric and -ε-caproic acids (I) and their esters were obtained by the reaction of N'-phenylbiguanide with the monoester chlorides of the corresponding dibasic acids – succinic, glutaric, adipic and pimelic acids.

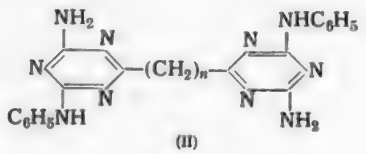


n = 2–5

(I)

Parallel with this we ran experiments on the condensation of N'-phenylbiguanide with the diesters of these acids. A study of the reaction products revealed that in the latter case, together with ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkylcarboxylic acids and their esters (the total yield of which does not exceed 45% of the theoretical), there is formed about 20% of ditriazines of general formula (II).

Replacement of one of the ester groups by the acid chloride group increases the total yield of the ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkylcarboxylic acid and its ester up to 70-89% and excludes the formation of the ditriazine (II). The yield of the monotriazines is increased substantially if the reaction is run with removal of the liberated water. Besides using ammoniacal copper sulfate solution to qualitatively test for the presence of starting N'-phenylbiguanide, the reaction course was also followed by the termination of water separation. The reaction rate and the yield of formed acids (I) and their esters were found to increase with increase in the length of the alkyl chain of the dibasic acid monoester chloride taken for reaction.



(II)

The obtained acids (I) are amphoteric compounds; they dissolve in alkalies with the formation of stable salts; their salts with acids on the amino group are easily hydrolyzed. The infrared absorption spectra, which confirmed the structure of the obtained triazinylalkylcarboxylic acids, revealed that apparently their molecule represents an internal salt; in this connection the ability to form salts decreases with increase in the length of the alkyl chain,

which is in agreement with our observation that the higher homologs show less acidic properties than do the lower homologs.

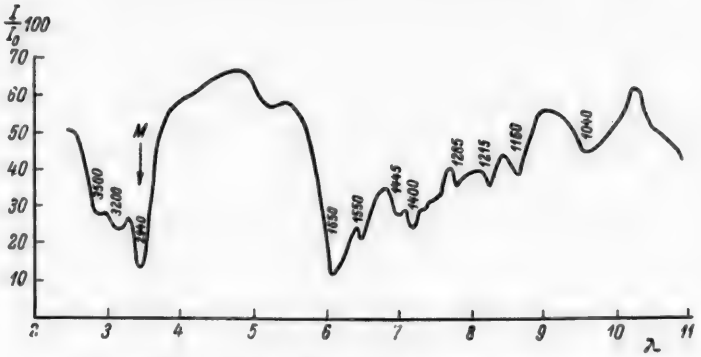


Fig. 1. Infrared absorption spectrum of β-(2-amino-4-phenylamino--1,3,5-triazin-6-yl)propionic acid (in vaseline oil).

When compared with the spectra of 2-amino-4-phenylamino-1,3,5-triazin-6-yl-carboxylic [1] and -acetic [2] acids, the spectrum of β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)propionic acid (Fig. 1) shows a reduced intensity of the absorption band lying in the 1400 cm^{-1} region, corresponding to the anionic form of the acid, and the appearance of bands of the free NH_2 group in the 1650 cm^{-1} region and of the OH group in the 3500 cm^{-1} region. Consequently, it appears that the triazinylpropionic acid exists not only as the internal salt, but also as the free acid.

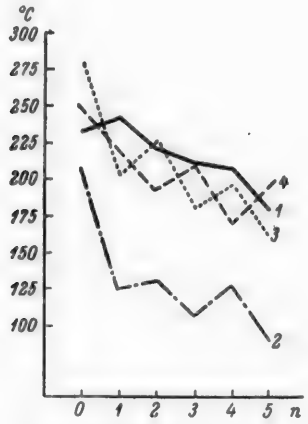


Fig. 2. Melting points of ω-(2--amino-4-phenylamino-1,3,5--triazin-6-yl)-alkylcarboxylic acids and their derivatives. 1) acids, 2) esters, 3) amides, 4) hydrazides.

The stability of the acids increases with increase in the length of the alkyl chain – γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyric, -δ-valeric and -ε--caproic acids do not lose carbon dioxide even when heated above their respective melting points.

The properties of acids (I) were also studied with respect to the carboxyl group – their acid chlorides, esters, amides and hydrazides were prepared. As can be seen from the presented diagram (Fig. 2), the esters, amides and hydrazides of these acids, the same as the acids themselves, represent crystalline substances, the melting points of which decrease in going from the lower to the higher homologs; in this connection the variation in the melting points shown by the amides and esters is the reverse of that shown by the hydrazides.

A number of the obtained compounds were tested in the Chemotherapy Division of VNIKhFI* as anti-infection agents, but all of the compounds proved to be inactive; the hydrazides showed only slight antituberculosis effect.

EXPERIMENTAL

β-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic Acid (I; n = 2)

Condensation of N'-Phenylbiguanide With Succinic Anhydride. To a warm solution of 10 g of N'-phenyl-

* All-Union Scientific-Research Chemical-Pharmaceutical Institute.

biguanide in 70 ml of dioxane was added 14 ml of 40 % sodium hydroxide solution, and then 6.5 g of succinic anhydride was added gradually at 60° with stirring; the stirring was continued for another 2 hours. The obtained precipitate was filtered, washed with alcohol, and dissolved in the minimum amount of water. The solution was acidified with dilute hydrochloric acid to pH 5; the obtained precipitate was filtered and washed with water. The β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid obtained in this manner was purified through the sodium salt – by disssolving in sodium bicarbonate solution and then acidifying with acetic acid solution until weakly acid to litmus. Yield 6.8 g (46.5 %). Needles (from water) with m.p. 219-220° (decomp.), soluble in sodium bicarbonate solution and in acid solutions at pH below 4, and difficultly soluble in water and alcohol.

Found %: C 55.41; H 5.10; N 26.76. M 256 (Rast). $C_{12}H_{13}O_2N_5$. Calculated %: C 55.59; H 5.02; N 27.02. M 259.

Condensation of N'-Phenylbiguanide With Diethyl Succinate. A mixture of 9.5 g of N'-phenylbiguanide, 15 ml of diethyl succinate, 50 ml of anhydrous alcohol and a solution of sodium alcoholate (0.5 g of Na in 15 ml of anhydrous alcohol) was heated at the boil under reflux for 10 hours. The obtained precipitate was filtered, washed with alcohol, and dissolved in water. The insoluble portion was filtered and recrystallized from a large volume of 75 % alcohol. Rhombic crystals with sharp edges, m.p. 269-270°; practically insoluble in water and organic solvents even when heated. Yield of 1',2'-bis-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-ethane 2.2 g (20 %).

Found %: C 59.73, 59.68; H 5.12, 5.21; N 34.72. M 386.7 (Rast). $C_{20}H_{20}N_{10}$. Calculated %: C 60.00; H 5.00; N 35.00. M 400.

The water solution was acidified with acetic acid to pH 5, and the obtained precipitate filtered and washed with water. Weight of β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid 1 g (7.2 %), m.p. 217-219° (decomp.). The alcoholic filtrate was evaporated in vacuo. The residue, an oily substance, gradually crystallized. The yield of ethyl β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionate was 6 g (37.5 %). Leaflets (from 75 % alcohol) with m.p. 131-132°, soluble in alcohol, difficultly soluble in ether, and insoluble in water.

Found %: C 58.39; H 5.72; N 24.88, 24.67. $C_{14}H_{17}O_2N_5$. Calculated %: C 58.53; H 5.92; N 24.39.

Ethyl Ester. To a mixture of 15 g of N'-phenylbiguanide, 10.7 g of anhydrous soda and 200 ml of anhydrous toluene was added with stirring a solution of 15 ml of succinic acid monoethyl ester chloride in 50 ml of anhydrous toluene at 60-65°. After all of the acid chloride had been added the temperature of the mixture was gradually raised to the boil, and stirring was continued for 20 hours. The reaction mass, cooled to 80°, was treated with 50 ml of hot anhydrous alcohol. The sodium chloride was filtered, and the filtrate was evaporated in vacuo to 1/3 volume. The resulting precipitate was filtered, washed with a small amount of toluene, and recrystallized from 75 % alcohol (1 : 7). The yield of ethyl β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionate was 10.5 g (42 %). M. p. 130-132°. We isolated 3.1 g of unreacted N'-phenylbiguanide from the filtrate.

Methyl Ester. To a mixture of 45 g of N'-phenylbiguanide, 45 g of fused potash and 500 ml of anhydrous toluene, contained in a flask with a Dean–Stark attachment, was added in drops and with stirring a solution of 46.5 g of succinic acid monoethyl ester chloride in 200 ml of anhydrous toluene at 65-68°. After all of the acid chloride had been added the temperature was raised to toluene boil, and the stirring was continued for 17.5 hours. The amount of water removed in this time was 5 ml. The reaction mass was cooled, and 200 ml of water was added to dissolve the potassium chloride and excess potash. The undissolved portion was filtered, combined with the precipitate obtained in the evaporation of the toluene mother liquor, and the whole recrystallized from 75 % alcohol (1 : 10). We obtained 38 g (55 %) of methyl β-(2-amino-4-phenylamino-1,3,5-traizin-6-yl)-propionate with m.p. 122-124°. Tiny needles, readily soluble in alcohol, less readily in ether, and insoluble in water.

Found %: N 25.38, 25.23. $C_{13}H_{15}O_2N_5$. Calculated %: N 25.64.

Acidification of the aqueous mother liquor with acetic acid to pH 5 gave β-(2-amino-4-phenylamino--1,3,5-triazin-6-yl)-propionic acid as a gelatinous precipitate, which gradually became crystalline. The acid was purified through the sodium salt. Yield 3.3 g (5 %). M. p. 219-221° (decomp.). After saponifying 15 g of the methyl ester by boiling with 50 ml of 8 % potassium hydroxide solution in methyl alcohol for 3 hours the formed potassium salt of the acid was filtered, dissolved in water, and the solution acidified with acetic acid to pH 5. The gel that separated at the start gradually became crystalline, and the crystals were filtered and washed with water. Yield of β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid 13 g (91.5 %). For purification the acid was dissolved in sodium bicarbonate solution and then precipitated by the addition of acetic acid to pH 5. M. p. 219-220°.

Amide. a) A mixture of 5 g of ethyl β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid, 25 ml of methyl alcohol and 25 ml of 28 % ammonia solution in methyl alcohol was shaken for 30 hours to dissolve the precipitate. The precipitate that separated after 2 days was filtered and washed with a small amount of alcohol. Yield 3.7 g (83 %). M.p. 225-226° (from 50 % alcohol). Needles, difficultly soluble in alcohol and water, and insoluble in ether.

Found %: C 55.92, 56.18; H 5.62, 5.61; N 32.21. $C_{12}H_{14}ON_6$. Calculated %: C 55.81; H 5.42; N 32.56.

b) A mixture of 1 g of β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid, 25 ml of anhydrous benzene and 1 g of phosphorus pentachloride were removed in vacuo. To the residue — a yellow viscous oil — was added with stirring and cooling 10 ml of 14% aqueous ammonia solution. The white precipitate obtained here was filtered, washed with water, and recrystallized from 75% alcohol. Yield of amide 0.45 g (44 %). M. p. 224-226°.

Hydrazide. A mixture of 5 g of ethyl β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionate, 2 ml of hydrazine hydrate and 10 ml of alcohol was heated at the boil for 3 hours. The obtained precipitate was filtered, washed with alcohol, and then with ether. Yield of hydrazide 3.7 g (78.7 %). M.p. 192-193° (from alcohol). Elongated thin plates, difficultly soluble in alcohol, and insoluble in water and ether.

Found %: C 52.65, 52.82; H 5.42, 5.38; N 35.44, 35.59. $C_{12}H_{15}ON_7$. Calculated %: C 52.74; H 5.49; N 35.89.

Monomethyl Succinate Diethylamide. To a solution of 35 ml of diethylamine in 100 ml of anhydrous benzene was added in drops at 20°, with stirring, a solution of 20 g of monomethyl succinate chloride in 30 ml of anhydrous benzene. After all of the chloride had been added the temperature was raised to 50° and stirring was continued at this temperature for 1 hour. The reaction mass was cooled and the obtained precipitate of diethylamine hydrochloride was filtered; the filtrate was washed with dilute hydrochloric acid, then with soda solution, and finally with water until neutral to litmus. The benzene solution was dried over sodium sulfate. After removal of the solvent the monomethyl succinate diethylamide was vacuum-distilled, b.p. 145-146° at 12 mm. Yield 18 g (72.6 %).

Found %: N 7.31, 7.12. $C_9H_{17}O_3N$. Calculated %: N 7.00.

The diethylamide of monoethyl succinate was obtained in a similar manner. B. p. 153-154° (12 mm).

Found %: N 6.90, 6.85. $C_{10}H_{19}O_3N$. Caclulated %: N 6.96.

Diethylamide of β-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic Acid. A mixture of 7 g of N'-phenylbiguanide, 9 g of the diethylamide of monomethyl succinate and 15 ml of anhydrous butyl alcohol was heated at the boil under reflux for 5 hours. The major portion of the alcohol was vacuum-distilled; the oily residue after standing for several days deposited a precipitate, which was purified by repeated recrystallization from small volumes of 75% methyl and 96% ethyl alcohols. Yield 5 g (40.3%). M.p. 142-143°. The diethylamide is soluble in alcohol, water and ether.

Found %: C 61.09; H 7.16; N 26.26, 26.96. $C_{16}H_{22}ON_6$. Calculated %: C 61.14; H 7.01; N 26.75.

The hydrochloride of the diethylamide was obtained by dissolving the free base in a minimum amount of anhydrous alcohol and adding dry ether, saturated with hydrogen chloride. The hydrochloride precipitate was washed with a mixture of alcohol and ether. M.p. 180.5-181.5° (from alcohol). Readily soluble in water and alcohol, and insoluble in ether.

Found %: C 54.12, 54.61; H 6.48, 6.63; Cl 10.36, 10.30. $C_{16}H_{22}ON_6 \cdot HCl$. Calculated %: C 54.77; H 6.56; Cl 10.12.

2-Diethylaminoethyl β-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-propionate Dihydrochloride. To 10 g of dry, finely ground potassium salt of β-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid was added with stirring a solution of 13 g of freshly distilled 2-diethylaminoethyl chloride in 150 ml of anhydrous benzene. The mixture was stirred for 12 hours at 65°. The potassium chloride precipitate was filtered. The benzene and unreacted diethylaminoethyl chloride were vacuum-distilled. The residual thick yellow oil was dissolved in a mixture of alcohol and ether and the solution was treated with ether that had been saturated with hydrogen chloride. The resulting fine white precipitate was filtered rapidly and washed with absolute ether. The yield of the dihydrochloride was 8 g (55 %). Hygroscopic substance, not melting up to 300°, soluble in water, and more difficultly soluble in alcohol.

Found %: Cl 15.91. $C_{18}H_{26}O_2N_6 \cdot 2$ HCl. Calculated %: Cl 15.99.

γ-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-butyric Acid (I; n = 3)

Ethyl Ester. To a mixture of 25 g of N'-phenylbiguanide, 400 ml of anhydrous toluene and 30 g of fused potash at 65-70° was added in drops and with stirring a solution of 30 g of monoethyl glutarate chloride in 100 ml of anhydrous toluene. After the addition the temperature was raised to mixture boil and the stirring was continued for 30 hours. The reaction mass was filtered hot; the major portion of the toluene was vacuum-distilled. The obtained precipitate was recrystallized from 75% alcohol (1 : 7). Yield of ethyl γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyrate 28.5 g (68%). M. p. 106.5-108°. Elongated leaflets, insoluble in water, difficultly soluble in ether, and soluble in other organic solvents.

Found %: N 23.20, 23.20. $C_{15}H_{19}O_2N_5$. Calculated %: N 23.25.

The precipitate that was insoluble in the hot toluene was dissolved in water and the water solution was acidified with acetic acid to pH 5. The precipitated γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyric acid was recrystallized from 75 % alcohol (1 : 50). Yield 8 g (21 %). M. p. 208.5-209.5°. Fine soft needles, soluble in sodium bicarbonate solution and in acid solutions at pH below 4, difficultly soluble in alcohol and water, and insoluble in ether.

Found %: C 57.05, 56.86; H 5.24, 5.36; N 25.52, 25.49. $C_{13}H_{15}O_2N_5$. Calculated %: C 57.14; H 5.49; N 25.64.

Condensation of N'-Phenylbiguanide with Diethyl Glutarate. A mixture of 10 g of N'-phenylbiguanide, 11 g of diethyl glutarate, 50 ml of anhydrous alcohol and a solution of sodium alcoholate (0.5 g of sodium metal in 10 ml of anhydrous alcohol) was heated under reflux for 6 hours. The precipitate obtained here was filtered and dissolved in water. The insoluble portion was recrystallized from a large volume of 75 % alcohol. Yield of 1',3'-bis-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propane 2.4 g (20.6 %). Prisms with m.p. 234-235°, practically insoluble in water and organic solvents.

Found %: C 61.12, 61.22; H 5.18, 4.97. M 398 (Rast). $C_{21}H_{22}N_{10}$. Calculated %: C 60.87; H 5.31. M 414.

Acidification of the aqueous filtrate gave 0.9 g (6 %) of γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyric acid with m.p. 208-209°. Evaporation of the alcoholic filtrate gave 6.2 g (38.8%) of ethyl γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyrate with m.p. 106.5-108°.

Saponification of the Ethyl Ester. A mixture of 10 g of ethyl γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyrate and 28 ml of 8 % alcoholic potassium hydroxide solution was heated at the boil under reflux for 3 hours. The precipitate obtained on cooling the mixture was filtered, and the filtrate was evaporated in vacuo. The precipitates were combined, and the potassium salt of the acid was dissolved in water. Acidification of the water solution with acetic acid to pH 5 gave γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyric acid as a precipitate, which was purified by dissolving in sodium bicarbonate solution and precipitating with acetic acid, and then recrystallizing from 75 % alcohol (1 : 50). Yield 8.1 g (90 %). M. p. 208.5-209.5°.

Amide. A mixture of 5.5 g of ethyl γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyrate, 25 ml of methyl alcohol and 25 ml of 25% ammonia solution in methyl alcohol was shaken for 15 hours until all of the precipitate had dissolved. The solution was allowed to stand for 15 days at room temperature. The obtained precipitate was filtered, washed with a small amount of alcohol, and then with ether. Yield 4 g (82 %). M. p. 179.5-180.5° (from 75% alcohol). Elongated plates, soluble in alcohol, and insoluble in water and ether.

Found %: N 30.16, 30.30. $C_{13}H_{16}ON_6$. Calculated %: N 30.88.

Hydrazide. A mixture of 6 g of ethyl γ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butyrate, 3 ml of hydrazine hydrate and 10 ml of anhydrous alcohol was heated at the boil under reflux for 2 hours. The precipitate obtained on cooling was filtered and recrystallized from 75 % alcohol (1 : 30). Yield 5.2 g (91.2 %). M. p. 208-209°. Fine needles, difficultly soluble in alcohol, very slightly soluble in water, and insoluble in ether.

Found %: C 54.95, 55.01; H 5.92, 6.12; N 34.20. $C_{13}H_{17}ON_7$. Calculated %: C 54.35; H 5.92; N 34.11.

δ-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-valeric Acid (I; n = 4)

Condensation of N'-Phenylbiguanide With Diethyl Adipate. To a solution of 32 g of diethyl adipate in 20

ml of anhydrous alcohol was added a solution of sodium alcoholate (3 g of sodium metal in 50 ml of anhydrous alcohol), and then a warm solution of 22 g of N'-phenylbiguanide in 50 ml of anhydrous alcohol was added gradually, after which the whole mixture was heated at the boil for 4 hours. The obtained precipitate was filtered. Evaporated of the alcohol filtrate gave 10 g (25.6 %) of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)--valerate. Recrystallization from alcohol gave plates with m.p. 126-127°.

Found %: N 22.69, 22.45. $C_{16}H_{21}O_2N_5$. Calculated %: N 22.22.

The precipitate obtained from the condensation was dissolved in water. The insoluble portion was filtered and then recrystallized from a large volume of 75 % alcohol. Yield of 1',4'-bis-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butane 6 g (22.5 %). Prisms with m.p. 229-230°, and very difficultly soluble in water and organic solvents.

Found %: C 61.52, 61.32; H 5.61, 5.75. M 410 (Rast). $C_{22}H_{24}N_{10}$. Calculated %: C 61.68; H 5.61. M 428.

The dihydrochloride of 1',4'-bis-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-butane was obtained as plates with m.p. 226-228°.

Found %: C 52.44, 52.40; H 5.20, 5.23; N 28.00, 28.04; Cl 13.88. $C_{22}H_{24}N_{10} \cdot 2HCl$. Calculated %: C 52.69; H 5.19; N 27.94; Cl 14.17.

The water solution was acidified with acetic acid to pH 5. Here the δ-(2-amino-4-phenylamino-1,3,5--triazin-6-yl)-valeric acid deposited as a viscous mass, which solidified the next day. Recrystallization from a large volume of 75 % alcohol gave 6 g (17 %) of substance with m.p. 206-207°. Colorless leaflets, difficultly soluble in alcohol, water and dioxan , and insoluble in ether; soluble in sodium bicarbonate solution and strong acids.

Found %: C 58.88, 58.74; H 6.15, 6.36; N 23.95, 24.30. $C_{14}H_{17}O_2N_5$. Calculated %: C 58.53; H 5.92; N 24.39.

The ethyl ester of δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeric acid was obtained in the same m manner as the methyl ester of ℓ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic acid. From 50 g of N'--phenylbiguanide, 700 ml of anhydrous toluene, 22 g of fused potash and 57.5 g of monoethyl adipate chloride in 200 ml of anhydrous toluene we obtained 60 g (67.4 %) of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valerate, m.p. 126-127°. Leaflets, readily soluble in alcohol and ether, and insoluble in water.

Acidification of the water layer with acetic acid until weakly acid to litmus gave 0.5 g of δ-(2-amino-4--phenylamino-1,3,5-triazin-6-yl)-valeric acid; after purification through the sodium salt, m.p. 206-207°.

The monoacetyl derivative of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valerate had m.p. 155-156° (from 75 % alcohol).

Found %: N 19.50, 19.46. $C_{18}H_{23}O_3N_5$. Calculated %: N 19.59.

The diacetyl derivative of the ethyl triazinylvalerate had m.p. 90-91° (from 50 % alcohol).

Found %: N 17.65, 17.50. $C_{20}H_{25}O_4N_5$. Calculated %: N 17.53.

The saponification of 25 g of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valerate with 100 ml of 6 % alcoholic potassium hydroxide solution at the boil for 3 hours gave δ-(2-amino-4-phenylamino-1,3,5--triazin-6-yl)-valeric acid as a thick viscous white oil, which gradually solidified. It was purified through the sodium salt, followed by recrystallization from 80 % alcohol (1 : 40). Yield 22.5 g (82 %). M. p. 206-207°. Colorless leaflets, difficultly soluble in alcohol, water and dioxan , and insoluble in ether.

The hydrochloride of δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeric acid was obtained by adding in alcohol solution of hydrogen chloride to a warm alcohol solution of the free base. Leaflets with m.p. 220.5-222° (decompn.) (from anhydrous alcohol).

Found %: Cl 11.20. $C_{14}H_{17}O_2N_5 \cdot HCl$. Calculated %: Cl 11.00.

Methyl Ester. A mixture of 1 g of the triazinylvaleric acid and 10 ml of anhydrous methyl alcohol in the presence of 0.5 ml of concentrated sulfuric acid was heated at the boil under reflux for 4 hours. Then nearly all of the alcohol was removed, and the cooled residue was treated with diethyl ether and soda solution until weakly

alkaline to litmus . The ther solution was dried over sodium sulfate, the ether was removed by distillation, and the methyl ester of δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeric acid was recrystallized from 75 % methyl alcohol (1 : 10). Yield 1 g (95 %). Microscopic needles with m.p. 122-123.5 readily soluble in alcohol and ether, and insoluble in water.

Found %: N 23.78, 23.88. $C_{15}H_{19}O_2N_5$. Calculated %: N 23.25.

The Hydrazide was obtained by boiling a mixture of 3 g of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin--6-yl)-valerate, 5 ml of hydrazine hydrate and 10 ml of anhydrous ethyl alcohol for 2 hours. After recrystallization from 75 % alcohol, m.p. 169-170°. Yield 2 g (70 %). Colorless leaflets, difficultly soluble in alcohol, and insoluble in water and ether.

Found %: N 32.10, 32.30. $C_{14}H_{19}ON_7$. Calculated %: N 32.56.

Amide. a) A mixture of 2 g of ethyl δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valerate and 30 ml of 19 % ammonia solution in methyl alcohol was shaken at 30° for 1 hour until all of the precipitate had dissolved. After standing for 20 days at room temperature the obtained precipitate was filtered and recrystallized from 75 % methyl alcohol. Yield 1.5 g (83 %). M. p. 195-196°. Colorless prisms, readily soluble in alcohol.

Found %: C 58.77, 59.24; H 6.40, 6.18; N 29.77. $C_{14}H_{13}ON_6$. Calculated %: C 58.74; H 6.29; N 29.37.

b) To 10 g of finely divided δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeric acid was added 150 ml of acetyl chloride, and then 13 g of ground phosphorus pentachloride was added with stirring. Stirring was continued for 3 hours at 40-50°. The next day the precipitate of δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)--valeric acid hydrochloride was filtered, washed with anhydrous benzene, and recrystallized from anhydrous alcohol. Weight 1 g, m.p. 220.5-222° (decompn.). The filtrate was vacuum-distilled to remove the acetyl chloride and phosphorus oxychloride, while the residue was δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeryl chloride, obtained as an amber-colored oil, which subsequently solidified to a brittle resin with a reddish color. Weight 10 g.

Three grams of the above obtained δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeryl chloride was added with stirring and cooling to 20 ml of 20 % aqueous ammonia solution. The white precipitate obtained here was filtered and recrystallized from alcohol. Yield of δ-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-valeramide 2.3 g (81 %). M. p. 195-196°.

ε-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-caproic Acid (I; n = 5)

The Ethyl Ester was obtained in the same manner as the methyl ester of β-(2-amino-4-phenylamino-1,3,5--triazin-6-yl)-propionic acid. From 15 g of N'-phenylbiguanide, 250 ml of anhydrous toluene, 12 g of fused potash and a solution of 23 g of monoethyl pimelate chloride in 100 ml of anhydrous toluene at 65-70°, after vacuum--distillation of the toluene, we obtained an oil, which after long standing in a vacuum-desiccator partially crystallized. It was pressed on porous plate and recrystallized from benzine (b.p. 70-80°). The yield of the ester was 18 g (71 %). M. p. 87.5-89.5°. Tiny needles, readily soluble in the usual organic solvents, and insoluble in water.

Found %: N 20.93, 21.02. $C_{17}H_{23}O_2N_5$. Calculated %: N 21.27.

The Acid was obtained by the saponification of 4 g of the ethyl ester with 10 g of a 5% alcoholic sodium hydroxide solution at the boil on the water for 3.5 hours. After cooling, the sodium salt of the acid was filtered and dissolved in a small volume of water. The water solution was acidified to pH 5 with acetic acid. The ε--(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-caproic acid separated as a white, viscous, thick mass, which subsequently solidified. Yield 3.13 g (87 %). M. p. 177.5-178° (from 90 % methyl alcohol). Microscopic needles, soluble in sodium bicarbonate solution and in strong acids, difficultly soluble in alcohol, practically insoluble in water, and insoluble in ether.

Found %: C 59.52, 59.91; H 6.11, 6.27; N 23.26. $C_{15}H_{19}O_2N_5$. Caculated %: C 59.80; H 6.31; N 23.25.

The Amide was obtained in the same manner as described above. Yield 80 %, m.p. 164-165° (from 50 % methyl alcohol). Leaflets, soluble in alcohol, and insoluble in water and ether.

Found %: N 27.66, 27.50. $C_{15}H_{20}ON_6$. Calculated %: N 28.00.

Hydrazide. Yield 79 %. M. p. 194.5-196° (from 75 % methyl alcohol). Elongated microscopic leaflets,

soluble in alcohol and hot water, and insoluble in ether.

Found %: C 57.18; H 6.52; N 31.00. $C_{15}H_{11}ON_7$. Calculated %: C 57.14; H 6.66; N 31.11.

SUMMARY

1. β-(2-Amino-4-phenylamino-1,3,5-triazin-6-yl)-propionic, -γ-butyric, -δ-valeric and -ε-caproic acids were obtained in good yields by the condensation of N'-phenylbiguanide with the chlorides of the monoethyl esters of succinic, glutaric, adipic and pimelic acids. As a result, the method developed by us for the preparation of 2-amino-4-phenylamino-1,3,5-triazin-6-yl-alkylcarboxylic acids from the chlorides of the monoesters of dibasic acids is a general method for the preparation of substituted 1,3,5-triazin-6-yl-carboxylic acids. The reaction rates and the yields of ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl-alkylcarboxylic acids increase in measure with increase in the chain length of the dibasic acid.

2. The stability of ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkylcarboxylic acids toward decarboxylation increases with increase in the length of the alkyl chain.

3. Based on the spectral data, the studied acids exist not only as internal salts, but also as the free acids. The capacity for internal salt formation decreases with increase in the length of the alkyl chain.

4. As the length of the alkyl chain is increased the melting points of the derivatives based on the carboxyl group show a reduction that can be depicted by a zigzag type of curve, in which connection the (variation) oscillation shown by the esters and amides is the reverse of that shown by the hydrazides.

5. The condensation of N'-phenylbiguanide with the diesters of dibasic acids is not well defined; together with the esters of ω-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkylcarboxylic acids there occurs the formation of bis-(2-amino-4-phenylamino-1,3,5-triazin-6-yl)-alkanes in up to 20 % of the theoretical amount.

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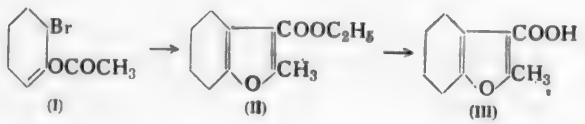
* Original Russian pagination. See C. B. Translation.

SOME PROPERTIES OF ENOL ACETATE

II. PREPARATION OF 2-METHYL-3-CARBETHOXY-4,5,6,7-TETRAHYDROCOUMARONE BY THE REACTION OF 3-BROMO-2-ACETOXY-1-CYCLOHEXENE WITH SODIOACETOACETIC ESTER

I. V. Machinskaya and V. A. Barkhash

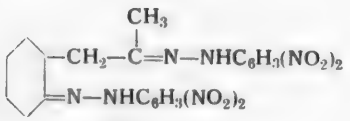
In the previous communication [1] we described the bromination of cyclohexanone enol acetate with N-bromosuccinimide, leading to the formation of 3-bromo-2-acetoxy-1-cyclohexene. In the present paper we studied the reaction of this brominated enol acetate (I) with sodioacetoacetic ester. The reaction was run with heating in alcohol medium. The main reaction product proved to be 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone (II), the best yield of which (74 %) was obtained using a 1 : 2 mole ratio of bromo derivative to acetoacetic ester and a temperature of 50-60°. The alkaline hydrolysis of (II) gave 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid (III) as colorless crystals with m.p. 161°, which agrees with the data given in the literature for this compound [2]. These transformations can be depicted by the following scheme



(I) (II) (III)

The formation of furan derivatives from the brominated enol acetates of ketones apparently proceeds with greater ease than when α-halo substituted ketones are used in an analogous reaction. Thus, according to Kuhn [2] the reaction of α-chlorocyclohexanone with sodioacetoacetic ester gave the ethyl ester of 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid in a yield of only 30.4 %.

The ethyl 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylate synthesized by us proved to be stable when heated with dilute acids. Thus, for example, we were unable to saponify this ester by heating it with 15 % hydrochloric acid for 10 hours. This apparently was due to steric hindrance, associated with the presence of a methyl group in the α-position to the carbethoxyl group. When heated with alcoholic sulfuric acid solution and 2,4-dinitrophenylhydrazine both the ester of 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid and the free acid give the bis-2,4-dinitrophenylhydrazone of α-acetonylcyclohexanone (IV), obtained as dark-red crystals with m.p. 211°.



(IV)

In the case of the ethyl ester of 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid we were unable to isolate the corresponding derivative of the diketo ester. Apparently, here saponification and decarboxylation proceed either before or simultaneously with the opening of the furan ring.

The method developed by us for the preparation of the ethyl ester of 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid from the brominated enol acetate of cyclohexanone can apparently be used for the synthesis of various other furan derivatives. In our opinion, this method is more convenient than the method of obtaining furan compounds from the difficultly available γ-diketones, and is also more convenient than the recently described method of obtaining furan derivatives from unsaturated ketones by reaction with perbenzoic acid and subsequent hydrolysis [3].

EXPERIMENTAL

Preparation of 2-Methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone. Into a three-necked flask, fitted with efficient stirrer, reflux condenser with calcium chloride, and dropping funnel, was charged 100 g of anhydrous alcohol and then 6.9 g of sodium metal, cut into small pieces, was added gradually. After the sodium had dissolved, to the mixture, with cooling and stirring, was added in drops 78 g of freshly distilled acetoacetic ester. Then to the cold solution was added dropwise in 1 hour 66 g of freshly distilled bromocyclohexenyl acetate with vigorous stirring, in which connection a heavy precipitate of sodium bromide was obtained. Then the mixture was heated on the water bath to 50-60° for 1 hour. The precipitate of sodium bromide was filtered and washed with alcohol; the alcohol was vacuum-distilled to dryness. The residue was dissolved in a small volume of water, repeatedly extracted with ether, and dried over sodium sulfate. The ether was distilled off and the residue was vacuum-distilled. The main portion distilled at 112-115° (1 mm). Yield 74 %.

n_D^{20} 1.4870, d^{20} 1.0842, MR 55.18; Calc. 55.46

Found %: C 68.88, 68.95; H 7.94, 7.84. Sapn. No. 252.3. $C_{12}H_{16}O_3$. Calculated %: C 69.20; H 7.74. Sapn. No. 269.0.

Alkaline Hydrolysis of Ethyl 2-Methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylate. Eight grams of 2-methyl--3-carbethoxy-4,5,6,7-tetrahydrocoumarone was boiled for 3 hours with excess 10 % alcoholic potassium hydroxide solution. Then carbon dioxide was bubbled into the mixture, the obtained precipitate filtered, and the alcohol vacuum-distilled to dryness. The residue was dissolved in water and the colored impurities were extracted once with ether. Acidification of the aqueous solution gave a friable crystalline product, which after recrystallization from methyl alcohol had m.p. 161°. The elementary analysis data and the acid number correspond to 2-methyl--3-carboxy-4,5,6,7-tetrahydrocoumarone.

Found %: C 66.30, 66.41; H 6.71, 6.77. Acid amount 305.8. $C_{10}H_{12}O_3$. Calculated %: C 66.64; H 6.71. Acid amount 310.1.

The yield of 2-methyl-4,5,6,7-tetrahydrocoumarone-3-carboxylic acid was 6.1 g (88%).

Reaction of 2-Methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone and 2-Methyl-3-carboxy-4,5,6,7-tetrahydrocoumarone with 2,4-Dinitrophenylhydrazine. Ten grams of 2,4-dinitrophenylhydrazine was dissolved in 2 ml of warm concentrated sulfuric acid and then diluted with 10 ml of anhydrous alcohol. A solution of 0.5 g of 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone in anhydrous alcohol was added at one time. The mixture was boiled on the water bath for several minutes. After cooling the dark-red precipitate was filtered, washed with anhydrous alcohol, and recrystallized from a mixture of ethyl alcohol and ethyl acetate; m.p. 211°.

Similar treatment of 2-methyl-3-carboxy-4,5,6,7-tetrahydrocoumarone gave a substance with the same melting point. The mixed melting point of the two substances was not depressed.

Found %: N 21.88, 21.95. $C_{21}H_{22}N_8O_8$. Calculated %: N 21.78.

SUMMARY

1. A method was developed for the preparation of 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone in 74 % yield by the reaction of 3-bromo-2-acetoxy-1-cyclohexene with sodioacetoacetic ester.

2. The alkaline hydrolysis of 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone gave 2-methyl-4,5,6,7--tetrahydrocoumarone-3-carboxylic acid.

3. It was established that the reaction of 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocoumarone, and also of 2-methyl-3-carboxy-4,5,6,7-tetrahydrocoumarone, with 2,4-dinitrophenylhydrazine gives the bis-2,4-dinitrophenylhydrazone of α-acetonylcyclohexanone.

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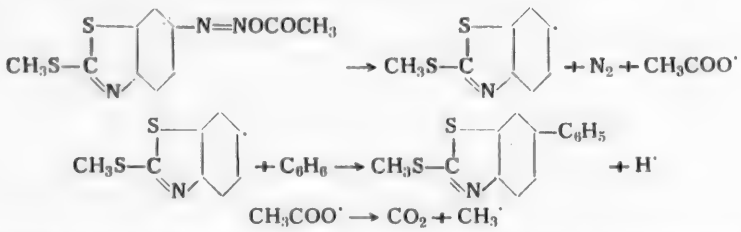
SYNTHESIS OF 2-METHYLMERCAPTO-6-PHENYL- AND 2-ETHYL-6-PHENYL-BENZOTHIAZOLES THROUGH DIAZO COMPOUNDS

I. K. Ushenko

In a previous communication [1] we had shown that various diazo compounds, when added to benzene, begin to decompose with the evolution of gaseous products and the formation of phenylbenzothiazoles. In the present paper we give the synthesis of diazo compounds from 2-methylmercapto-6-aminobenzothiazole and 2-ethyl-6--aminobenzothiazole, and also a study of their properties and transformations.

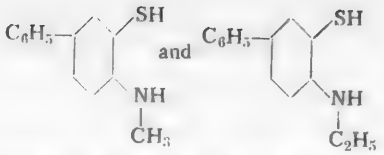
2-Methylmercapto-6-aminobenzothiazole is easily diazotized and forms the diazonium chloride, the solutions of which are colored a light-yellow and remain unchanged after standing for many hours in ice. The solution of the diazonium chloride, obtained from 2-methyl-6-aminobenzothiazole, assumes in 30-40 minutes a brownish-red color and gradually begins to decompose. As a result, the presence of a methylmercapto group in the 2 position of the benzothiazole ring increases the stability of the corresponding diazonium salt. 2-Methylmercaptobenzothiazolyl-6-diazoacetate is also stable, and it readily dissolves in benzene and slowly decomposes with the evolution of gaseous products and the formation of free benzothiazole radicals. The latter, reacting with the benzene, from 2-methylmercapto-6-phenylbenzothiazole in 70 % yield. Under similar conditions the diazonium chloride from 2-methyl-6-aminobenzothiazole gives 2-methyl-6-phenylbenzothiazole in 37% yield [1]. We also ran some experiments on the decomposition in benzene of other diazo compounds, obtained from 2-methylmercapto-6-aminobenzothiazole. Thus, the reaction of 2-methylmercaptobenzothiazolyl-6-diazotate with benzene gives 2-methylmercapto-6-phenylbenzothiazole in 39% yield, while the reaction of dry 2-methylmercaptobenzothiazolyl-6-diazoacetate and of 2-methylmercapto-6-nitrosoacetamidobenzothiazole with benzene gives 2-methylmercapto-6-phenylbenzothiazole in 38 and 43% yield, respectively. Considerably lower yields of 2--methyl-6-phenylbenzothiazole are obtained when the analogous diazo compounds of 2-methyl-6-aminobenzothiazole are reacted with benzene.

The decomposition of 2-methylmercaptobenzothiazolyl-6-diazoacetate in benzene and the formation of 2-methylmercapto-6-phenylbenzothiazole can be depicted by the scheme



A vigorous evolution of carbon dioxide and nitrogen was observed in the decomposition of the indicated diazoacetate and nitrosoacetamido derivative in benzene.

2-Methylmercapto-6-phenylbenzothiazole readily reacts with the methyl and ethyl esters of p-toluenesulfonic acid to give the corresponding quaternary salts in 90-92 % yield. These quaternary salts are cleaved by alcoholic alkali, in which connection the two aminothiophenols are obtained:



The low-melting aminothiophenols were analyzed as the disulfides. The same as other alkyl- and aryl-aminothiophenols [2, 3], they readily condense with carboxylic acid chlorides to give quaternary salts of 6-phenyl--2-alkylbenzothiazoles. Other methods for the synthesis of such compounds are associated with considerable difficulties. The quaternary salts of 2-alkyl-6-phenylbenzothiazoles can be used to synthesize cyanine dyes.

We also obtained several new diazo compounds from 2-ethyl-6-aminobenzothiazole and studied their properties. Thus, for example, the reaction of the diazotate, obtained from 2-ethyl-6-aminobenzothiazole, with cooled benzene gives 2-ethyl-6-phenylbenzothiazole in 35 % yield. 2-Ethylbenzothiazolyl-6-diazoacetate, the same as in other cases [1], gives a higher yield of 2-ethyl-6-phenylbenzothiazole, and specifically 46 %.

2-Ethylbenzothiazolyl-6-diazoacetate and 2-ethyl-6-nitrosoacetamidobenzothiazole were also obtained by us as solids. Both compounds are stable and can be kept for several days, but when introduced into dry benzene they slowly begin to decompose with the evolution of gaseous products and the formation of 2-ethyl-6-phenylbenzothiazole. Here 2-ethyl-6-phenylbenzothiazole is obtained in 29 % yield from 2-ethylbenzothiazolyl-6--diazoacetate, and in 50 % yield from 2-ethyl-6-nitroacetamidobenzothiazole.

The mechanism for the synthesis of 2-ethyl-6-phenylbenzothiazole through diazo compounds is similar to the mechanism for the synthesis of 2-methylmercapto-6-phenylbenzothiazole. In this case also we observed the evolution of carbon dioxide and nitrogen in the decompostiion of 2-ethylbenzothiazolyl-6-diazoacetate in benzene.

EXPERIMENTAL

2-Methylmercapto-6-phenylbenzothiazole can be obtained by four methods. 1st Method. A solution of 5.8 g of 2-methylmercapto-6-aminobenzothiazole in 21 ml of concentrated hydrochloric acid and 18 ml of water was cooled to -2° and diazotized with 2.5 g of sodium nitrate in 5 ml of water. After standing for 10 minutes the diazonium salt was mixed with 200 ml of thiophene-free benzene, cooled to 0°. The mixture was stirred and to it in 20-25 minutes was added 8.4 g of sodium hydroxide in 42 ml of water. The mass was stirred for 15 hours, then the solution was filtered, the benzene separated, the water layer extracted wtice with benzene, and the benzene removed completely by distillation. The residue, a dark-brown mass, was dissolved in chloroform and chromatographed on aluminum oxide. The colorless zone, representing the formed 2-methylmercapto-6-phenylbenzothiazole, shows a blue-violet fluorescence under ultraviolet light. The free base was eluted with benzene. A thick colorless oil was obtained, which crystallized on cooling. Yield 3 g (38.9%), m.p. 71-72°. After recrystallization from alcohol it was obtained as colorless mother-of-pearl leaflets with m.p. 73°.

Found %: N 5.44, 5.42; S 25.23, 25.30. $C_{14}H_{11}NS_2$. Calculated %: N 5.44; S 24.90.

2nd Method. A solution of 11.7 g of 2-methylmercapto-6-aminobenzothiazole in 42 ml of concentrated hydrochloric acid and 35 ml of water was cooled to -5° and diazotized with 4.9 g of sodium nitrite in 10 ml of water. The diazonium salt was mixed with 250 ml of benzene, cooled to 6°, and to the mixture was added in 35 minutes a solution of 63 g of sodium acetate in 100 ml of water. The flask contents were stirred for 20 hours. Further purification of the 2-methylmercapto-6-phenylbenzothiazole was accomplished in the same manner as indicated above. Yield 10.9 g (70 %), m.p. 71°. After recrystallization from alcohol, m.p. 73°.

3rd Method. The diazotization of 5.8 g of 2-methylmercapto-6-aminobenzothiazole was accomplished in the usual manner. To the cooled diazonium chloride, with stirring and cooling, was added a solution of 8.4 g of sodium hydroxide in 15 ml of water, and then 5.2 g of acetic anhydride. The brown-colored precipitate was filtered, washed with water, and dried in the air. Yield 3.7 g (46 %), m.p. 79° (with decompn.). The diazoacetate does not contain halogen, and is stable at room temperature. 5.3 g of ground 2-methylmercapto-benzothiazolyl-6-diazoacetate was added to 150 ml of dry benzene. A vigorous evolution of gaseous products began immediately, and the benzene became brown in color. After standing for 2 days the mixture was heated at 60° for 6 hours. The solution was filtered and worked up in the same manner as indicated in the 1st method. Yield of 2-methylmercapto--6-phenylbenzothiazole 2.2 g (43 %).

4th Method. To a solution of 9.5 g of 2-methylmercapto-6-acetamidobenzothiazole in 100 ml of glacial acetic acid and 6 ml of acetic anhydride was added 2 g of phosphorus pentoxide, the mixture cooled to 6-5°, and nitrogen oxides passed through the solution until a dark-green color appeared. The nitrogen oxides were obtained by the method described in [4]. Then the solution was poured into 300 ml of ice water, the precipitate of the nitrosoacetamido derivative filtered, washed with ice water, and then air-dried. Yield 4.5 g (84 %). 2-Methylmercaptobenzothiazolyl-6-nitrosoacetamide was obtained as yellow crystals, m.p. 134-136° with violent decomposition.

To 150 ml of dry benzene was added 5.3 g of 2-methylmercapto-6-nitrosoacetamidobenzothiazole. The evolution of gaseous products was observed and the benzene became yellow-colored. Further treatment was the same as indicated in the 3rd method. Yield 1.9 g (37 %), m.p. 73°. The synthesis of 2-methylmercapto-6-phenylbenzothiazole by the 2nd method is the simplest.

2-Methylmercapto-6-phenylbenzothiazole Methyl-p-toluenesulfonate. A mixture of 7.7 g (0.03 mole) of 2-methylmercapto-6-phenylbenzothiazole and 7.4 g (0.04 mole) of methyl p-toluenesulfonate was heated in an oil bath for 7 hours at 155-160°. The mass was ground, rubbed with benzene, and the precipitate filtered, washed with boiling benzene, and dried. Yield of quaternary salt 12.2 g (91 %).

2-Methylmercapto-6-phenylbenzothiazole Ethyl-p-toluenesulfonate. A mixture of 7.7 g of 2-methylmercapto-6-phenylbenzothiazole and 8 g of ethyl p-toluenesulfonate was heated for 10 hours at 160-165°. The solid mass was washed with dry acetone. Yield 12.7 g (92 %).

5-Phenyl-2-methylaminophenyl Mercaptan. To a solution of 13.2 g of 2-methylmercapto-6-phenylbenzothiazole methyl-p-toluenesulfonate in 30 ml of alcohol was added a solution of 20 g of potassium hydroxide in 70 ml of alcohol. The mixture was boiled on the water bath for 3.5 hours, the alcohol was distilled off, and the residue was dissolved in 100 ml of water; the complete solution of the potassium salt of the aminothiophenol was observed here. The solution was cooled and neutralized with hydrochloric acid. A light-yellow oil deposited, which crystallized after 3 hours. The precipitate was filtered, washed with cold water, and dried in a vacuum-desiccator over sulfuric acid. Yield 6.8 g (94 %), m.p. 47-48°.

5-Phenyl-2-ethylaminophenyl Mercaptan. To a solution of 13.7 g of 2-methylmercapto-6-phenylbenzothiazole ethyl-p-toluenesulfonate in 25 ml of alcohol was added a solution of 20 g of potassium hydroxide in 75 ml of alcohol. Yield 6.3 g (91 %), m.p. 35-36°.

5,5'-Diphenyl-2,2'-dimethylaminodiphenyl Disulfide. To a solution of 0.2 g of 5-phenyl-2-methylaminophenyl mercaptan in 5 ml of alcohol was added 15 ml of 2% hydrogen peroxide. After standing for 10 hours the precipitate was filtered, washed with water, dried, and recrystallized from alcohol. Tiny yellow tablets, m.p. 138-139°.

Found %: N 6.66, 6.55; S 14.84. $C_{26}H_{24}N_2S_2$. Calculated %: N 6.54; S 14.95.

5,5'-Diphenyl-2,2'-diethylaminodiphenyl Disulfide. A solution of 0.2 g of 5-phenyl-2-ethylaminophenyl mercaptan in 7 ml of methyl alcohol was treated with 15 ml of 2% hydrogen peroxide. Light-yellow crystals from alcohol, m.p. 124-125°.

Found %: N 6.18, 6.23; S 14.16, 14.22. $C_{28}H_{28}N_2S_2$. Calculated %: N 6.14; S 14.03.

2-Methyl-6-phenylbenzothiazole Methochloride. To a solution of 3.2 g of 5-phenyl-2-methylaminophenyl mercaptan in 10 ml of dry benzene was added a solution of 1.5 g of acetyl chloride in 5 ml of benzene. The mixture was heated to the boil, the benzene removed, and the residue dissolved in hot water, boiled with animal charcoal, filtered, and evaporated on the water bath. Yield 2.8 g (68%). The chloride was converted to the iodide by treatment with potassium iodide, m.p. 235-236°. The mixed melting point with the methiodide obtained from 2-methyl-6-phenylbenzothiazole was not depressed.

2-Ethyl-6-phenylbenzothiazole Methochloride. To a solution of 3.2 g of 5-phenyl-2-methylaminophenyl mercaptan in 10 ml of benzene was added a solution of 1.7 g of propionyl chloride in 7 ml of benzene. Yield of methochloride 3 g (70 %). The methiodide had m.p. 207-208°.

2-Methyl-6-phenylbenzothiazole Ethiodide. To a solution of 2.3 g of 5-phenyl-2-ethylaminophenyl mercaptan in 15 ml of benzene was added a solution of 1.2 g of acetyl chloride in 5 ml of benzene. The ethiodide was recrystallized from alcohol. Yield 2.6 g (70 %), m.p. 224-225°.

2-Ethyl-6-phenylbenzothiazole Ethiodide. To a solution of 2.3 g of 5-phenyl-2-ethylaminophenyl mercaptan in 15 ml of benzene was added a solution of 1.5 g of propionyl chloride in 10 ml of benzene. Yield 2.7 g (68 %), m. p. 183-184°.

2-Methoxymethyl-6-phenylbenzothiazole Ethiodide. To a solution of 2.3 g of 5-phenyl-2-ethylaminophenyl mercaptan in 15 ml of benzene was added a solution of 1.2 g of methoxyacetyl chloride in 8 ml of benzene. Yield 2.5 g (60 %). Light-yellow crystals (from alcohol), m.p. 179°.

2-Benzylbenzothiazole Ethiodide. A solution of 2.3 g of 5-phenyl-2-ethylaminophenyl mercaptan in 15 ml of benzene was mixed with a solution of 1.7 g of phenylacetyl chloride in 10 ml of benzene. Yield 2.1 g (45 %). Tiny light-yellow tablets (from alcohol), m.p. 183°.

2-Ethyl-6-phenylbenzothiazole can be obtained by four methods. 1st Method. A solution of 10.6 g of 2--ethyl-6-aminobenzothiazole in 15 ml of water and 20 ml of hydrochloric acid (d 1.19) was cooled to 0° and diazotized with 4.5 g of sodium nitrite in 8 ml of water. The benzothiazolyl diazonium chloride was added to 200 ml of benzene, contained in a flask and cooled to 6°. A solution of 8 g of sodium hydroxide in 20 ml of water was added in 35 minutes to the mixture with stirring. The mixture was stirred for 3 hours at 6°, and then for 12 hours at 20°. The flask contents were heated for 30 minutes on the boiling water bath, filtered, and the benzene separated and completely removed by distillation. The dark brown mass was dissolved in chloroform and chromatographed on aluminum oxide. The free base was eluted with benzene and recrystallized from methyl alcohol, m.p. 86-87°. Yield 5.07 g (35 %).

Found %: N 5.85, 5.79; S 13.18, 13.50. $C_{15}H_{13}NS$. Calculated %: N 5.85; S 13.39.

2nd Method. 2-Ethyl-6-aminobenzothiazole (10.6 g) was diazotized in the same manner as indicated above, and the diazonium salt solution was mixed with 200 ml of benzene, cooled to 6°. To the mixture with stirring was added 27 g of sodium acetate in 75 ml of water, Then the stirring was continued for 3 hours at 6°, and for 10 hours at 20°. Further treatment of the mixture was the same as indicated above. The light-yellow crystals were filtered from a thick oil. Yield of 2-ethyl-6-phenylbenzothiazole 5.3 g (37 %), m.p. 86-87°. The thick oil weighed 1.5 g (10 %); after long standing it crystallized almost completely; the crystals were filtered. Weight of crystals 1.1 g, weight of oil 0.2 g (2 %). The crystals proved to be 2-ethyl-6-phenylbenzothiazole, while the oily product proved to be 2-ethyl-benzothiazole. Total yield of 2-ethyl-6-phenylbenzothiazole 6.4 g (44%).

3rd Method. 2-Ethyl-6-aminobenzothiazole (5.3 g) was diazotized in the usual manner. To the cooled diazonium chloride with stirring was added a solution of 4 g of sodium hydroxide in 6 ml of water, and then 4.9 g of acetic anhydride. The brown-colored preicpitate was filtered, washed with water, and air-dried. Yield 3.5 g (47 %), m.p. 76° with decomposition. The diazoacetate does not contain halogen and is stable at room temperature.

To 200 ml of dry benzene was added 4.9 g of 2-ethylbenzothiazolyl-6-diazoacetate. Bubbles of gaseous products began to evolve instantly. After standing for 40 hours the mixture was heated for 6 hours at 65-70°. Then the solution was filtered and worked up in the same manner as indicated in the 1st method. Yield 1.1 g (23 %), m.p. 86-87°.

4th Method. To a solution of 8.8 g of 2-ethyl-6-acetamidobenzothiazole in 50 ml of glacial acetic acid and 6 ml of acetic anhydride was added 2 g of phosphorus pentoxide, the solution cooled to 5°, and then nitrogen oxides passed through the solution until a dark-green color appeared. The solution was poured into 150 ml of ice water and neutralized with soda. A yellow-orange oil deposited, which crystallized on standing. The precipitate of nitrosoacetamido derivative was filtered, washed with ice water, and dried in the air. Yield 7.2 g (71 %).

2-Ethylbenzothiazolyl-6-nitrosoacetamide was obtained as fairly unstable light-orange crystals, m.p. 77-78° with decomposition. To 150 ml of dry benzene was added 4.7 g of 2-ethylbenzothiazolyl-6-nitrosoacetamide. A vigorous evolution of gaseous products was observed, and the benzene assumed a brown color. After standing for 48 hours the flask contents were heated on the water bath for 7 hours at 70°. The solution after filtration was worked up in the same manner as indicated in the 1st method. Yield 2.5 g (50%), m.p. 86-87°.

The acetate method is the simplest of the four synthesis methods.

SUMMARY

1. The diazotate, diazoacetate and nitrosoacetamide were prepared from 2-methylmercapto-6-aminobenzothiazole. These diazo compounds decompose in benzene solution with the liberation of free benzothiazolyl radicals and the formation of 2-methylmercapto-6-phenylbenzothiazole.

2. 2-Methylmercapto-6-phenylbenzothiazole readily forms quaternary salts, which when treated with alcoholic alkali suffer cleavage with the formation of aminothiophenols. The obtained aminothiophenols condense with carboxylic acid chlorides toyield quaternary salts. Several 2-alkyl-6-phenylbenzothiazole quaternary salts were prepared.

3. Several diazo compounds were obtained from 2-ethyl-6-aminobenzothiazole, which when reacted with benzene gave 2-ethyl-6-phenylbenzothiazole.

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SYNTHESIS OF ARYLBENZOTHIAZOLES THROUGH TRIAZENES OF THE BENZOTHIAZOLE SERIES

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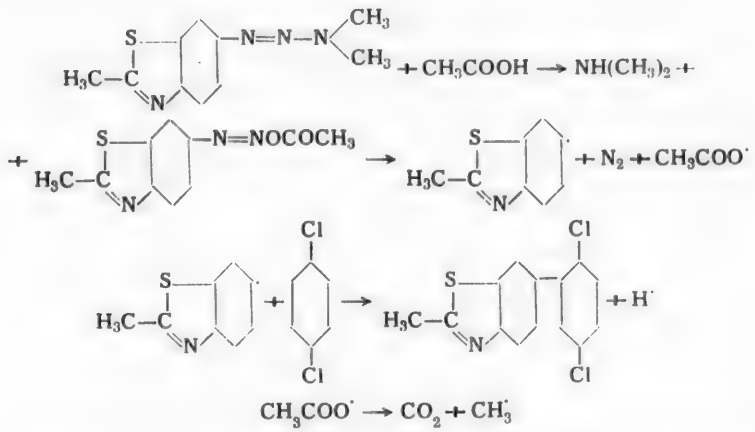
The synthesis of various arylbenzothiazoles by the reaction of dimethyltriazenes of the benzothiazole series with various aromatic compounds in the presence of glacial acetic acid is discussed in the present paper. The following triazenes were taken: 2-methylbenzothiazolyl-5-dimethyltriazene, 2-methylbenzothiazolyl-6-dimethyltriazene, 2-methylmercaptobenzothiazolyl-6-dimethyltriazene and 2-methylmercaptobenzothiazolyl-6-diethyltriazene. Instead of the dimethyltriazenes, it was found that the benzothiazolyldiethyltriazenes, the preparation of which is much simpler, could be successfully used in the synthesis of the arylbenzothiazoles. The yields of the arylbenzothiazoles are not reduced when this is done.

The aromatic compounds (component B) were taken in very large excess. As component B we used the following compounds: p-dichlorobenzene, dimethyl ether of hydroquinone, p-xylene and mesitylene. The indicated compounds when reacted with triazenes of the benzothiazole series for arylbenzothiazoles of definite structure, whereas the monosubstituted derivatives of benzene give a mixture of isomers, which makes it necessary to separate and establish the structure of the isolated products.

The mechanism for the synthesis of arylbenzothiazoles through the benzothiazolyldimethyltriazenes is probably as follows. When reacted with glacial acetic acid the triazenes from diazoacetates, which, found dissolved in an aromatic compound, decompose with the liberation of free benzothiazolyl radicals. The latter, reacting with the solvent, form arylbenzothiazoles.

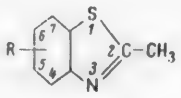


The evolution of nitrogen and carbon dioxide can be offered as evidence in support of such a mechanism. The evolution of carbon dioxide can be explained only by the temporary existence of neutral acetate radicals, since the acetate ion never loses carbon dioxide at room temperature, except in the case of anodic discharge. The reaction of benzothiazolyldimethyltriazenes with p-dichlorobenzene and with the dimethyl ether of hydroquinone yields a small amount of 2-methylbenzothiazole. The presence of 2-methylbenzothiazole in the reaction products can be explained by the reaction of benzothiazolyl radicals with hydrogen. The amount of 2-methylbenzothiazole

increases sharply (up to 24 %) if either p-xylene or mesitylene is used as the B component. This can probably be explained by the presence of steric hindrance, making it difficult for the benzothiazolyl radicals to approach the mesitylene or p-xylene molecule.

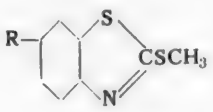
The 2-methylarylbenzothiazoles (Table 1) and 2-methylmercaptoarylbenzothiazoles (Table 2) synthesized by us are listed in the tables. The obtained bases are readily soluble in hot concentrated hydrochloric acid, much less soluble in dilute acid, and are very soluble in most organic solvents.

TABLE 1



Substance No.	R	Yield (in %)	Melting point	
			of the substance	of the picrate
(I)	6-p-Dichlorophenyl	42	91-92°	146°
(II)	6-p-Dimethoxyphenyl	53	106-107	184
(III)	6-p-Xylyl	29	oil	151
(IV)	6-Mesityl	12	75-76	167
(V)	5-p-Dichlorophenyl	26	110-111	156-157
(VI)	5-p-Dimethoxyphenyl	22	56-57	170-171
(VII)	5-p-Xylyl	31	41-42	163
(VIII)	5-Mesityl	14	73-74	176-177

TABLE 2



Substance No.	R	Yield (in %)	Melting point	
			of the substance	of the picrate
(IX)	p-Dimethoxyphenyl	56	98-100°	125-126°
(X)	p-Xylyl	37	oil	79-80
(XI)	Mesityl	14	43-44	114

When heated with ethyl p-toluenesulfonate or diethyl sulfate the new 2-methylarylbenzothiazoles readily form quaternary salts, and the latter form cyanine dyes.

EXPERIMENTAL*

2-Methylbenzothiazolyl-6-dimethyltriazene. Into a three-necked flask, fitted with stirrer, thermometer and dropping funnel, and immersed in a cooling bath, was charged 40.5 g (0.382 mole) of anhydrous sodium acetate in 225 ml of water and then at -2° was added 14.4 g (0.165 mole) of a 93.4% water solution of dimethylamine hydrochloride. To the mixture with stirring and cooling was then added in 15 minutes the diazonium chloride, obtained by the diazotization of 14.76 g of 2-methyl-6-aminobenzothiazole in 30 ml of hydrochloric acid and 23

* L. I. Chovnik and R. A. Lysenko participated in the experimental work.

ml of water with 6.6 g of sodium nitrite in 10 ml of water. The reaction mixture was stirred for 1 hour at -2°. The precipitate was filtered, washed with water, dried in the air, dissolved in 120 ml of chloroform, the solution filtered, the chloroform distilled off, and the residual mass crystallized. The triazene was dissolved in petroleum ether, the solution filtered from tar, and the solvent removed completely by distillation. Yield 16.3 g (83 %), m.p. 71-74°. Recrystallization from petroleum ether gave 12 g (61 %) of yellow-orange crystals with m.p. 74-75°.

2-Methylbenzothiazolyl-5-dimethyltriazene. 2-Methyl-5-aminobenzothiazole (49.2 g) was dissolved in 100 ml of hydrochloric acid (d 1.19) and 75 ml of water. The solution was cooled to -10°, and the thick mass of crystals was diazotized with 22 g of sodium nitrite in 35 ml of water. The diazo solution was kept at -5° for 10 minutes, and then it was poured with stirring into a cooled to -2° solution of 172 g of anhydrous sodium acetate in 750 ml of water, to which 62 ml of a 93.4% water solution of dimethylamine hydrochloride had previously been added at -2°. The mixture was stirred for 1.5 hours at -2°. The compound was recrystallized from petroleum ether. Yield 51.5 g (78 %). Tiny light-orange tablets, m.p. 110-111°.

2-Methylmercaptobenzothiazolyl-6-dimethyltriazene was obtained in a similar manner from 2-methylmercapto-6-aminobenzothiazole. The yield of the triazene was 96 %, m.p. 71-73°.

2-Methylmercaptobenzothiazolyl-6-diethyltriazene was obtained by the described method from 2-methylmercapto-6-aminobenzothiazole and diethylamine. Yield 81 %, m.p. 52-55°. Recrystallization from petroleum ether gave a 62 % yield of orange crystals with m.p. 55°.

Found %: N 19.70, 19.87. $C_{12}H_{16}N_4S_2$. Calculated %: N 19.31.

2-Methylmercapto-6-phenylbenzothiazole. A solution of 6.45 g of 2-methylmercaptobenzothiazolyl-6--diethyltriazene in 150 ml of dry benzene and 20 ml of glacial acetic acid was boiled for 12 hours, after which the reaction mixture was washed with water. The benzene was removed completely by distillation, and the precipitate was dissolved in chloroform and chromatographed on aluminum oxide. Two zones were formed in the column (from top to bottom): 1) a brown zone, not eluted with chloroform, and 2) a yellow zone, showing blue fluorescence under ultraviolet light. This zone was eluted with benzene. The benzene was distilled off, and the residual light-yellow oil crystallized. The base was recrystallized from methanol. Yield 3.65 g (62 %), white scales, m.p. 74-75°.

2-Methyl-6-p-dichlorophenylbenzothiazole (I). 2-Methylbenzothiazolyl-6-dimethyltriazene (11 g) was dissolved in 250 g of p-dichlorobenzene and 45 ml of glacial acetic acid (b.p. 118°) with heating. The mixture was heated at 100-110° for 15 hours. The vigorous evolution of gaseous products (nitrogen and carbon dioxide) was observed during the heating. Then 120 ml of concentrated hydrochloric acid was added to the mixture, and the mixture was boiled and then rapidly cooled with stirring. The p-dichlorobenzene that separated here was filtered and again treated as indicated above. The hydrochloric acid solution was neutralized under cooling with 15 % sodium hydroxide. The brown-colored precipitate was filtered, dried, dissolved in chloroform, and chromatographed on aluminum oxide. The colorless zone, formed by the base, was eluted with chloroform, the chloroform distilled off, and the residue made to crystallize by cooling. The base was recrystallized from methanol. Yield 6.3 g (42 %). Tiny colorless tablets, m.p. 91-92°.

Found %: Cl 24.20, 24.21. $C_{14}H_9NSCl_2$. Calculated %: Cl 24.14.

The picrate was obtained by mixing hot alcoholic solutions of the base and picric acid. Recrystallization from alcohol gave tiny yellow tablets.

Found %: N 10.85, 10.87. $C_{20}H_{12}O_7N_4SCl_2$. Calculated %: N 10.70

2-Methyl-6-p-dimethoxyphenylbenzothiazole (II). This compound was obtained in a similar manner from a mixture of 11 g of 2-methylbenzothiazolyl-6-dimethyltriazene, 250 g of hydroquinone dimethyl ether and 50 ml of glacial acetic acid. The mixture was heated at 80-90° for 15 hours. The base was isolated in the same manner as indicated above, and then was chromatographed twice on aluminum oxide. Benzene was used for the elution. A colorless oil was obtained, which crystallized on cooling. It was found that the base contained hydroquinone dimethyl ether, for which reason it was purified. The product was dissolved in the cold in 50 ml of concentrated hydrochloric acid, and here the evolution of heat was observed. After standing for 5 hours the deposited hydroquinone dimethyl ether was filtered and washed with strong hydrochloric acid. Weight 1.7 g. The hydrochloric acid was neutralized under cooling with ammonia. A light-yellow oil deposited, which crystallized in dense lumps. The precipitate was ground, washed with water, dried in the air, and recrystallized from methyl

alcohol. Yield 7.5 g (53 %). Colorless plates.

Found %: S. 11.25, 11.39. $C_{16}H_{15}O_2NS$. Calculated %: S 11.22.

The picrate of the base was obtained as yellow prisms.

Found %: N 10.74, 10.77. $C_{22}H_{18}O_9N_4S$. Calculated %: N 10.89.

2-Methyl-6-p-xylylbenzothiazole (III) was obtained by two methods. 1st Method. A solution of 9.8 g of 2-methyl-6-aminobenzothiazole in 20 ml of concentrated hydrochloric acid and 15 ml of water was diazotized with 4.4 g of sodium nitrite in 7 ml of water. Then the diazonium salt was mixed with 200 ml of p-xylene, cooled to +15°. Then to the mixture with stirring was added in 25 minutes a solution of 27 g of sodium acetate in 80 ml of water. The mixture was stirred at +15° for 3 hours, and then at 20° for 8 hours. The solution was filtered, the p-xylene was steam-distilled, and the viscous dark mass was dissolved in chloroform and chromatographed on aluminum oxide. The base was eluted with benzene. The zone, formed by the base, fluoresces with a blue light under ultraviolet light. Removal of the solvent by distillation gave the base as a viscous colorless oil. Yield 1.3 g (8.6%).

The reactants were taken in double amount in the second experiment. The yield of the base was 2.8 g (9%). The picrate was prepared from the base and picric acid. After recrystallization from alcohol it was obtained as tiny yellow tablets.

Found %: N 11.64, 11.42. $C_{22}H_{18}O_7N_4S$. Calculated %: N 11.61.

2nd Method. A solution of 11 g of 2-methylbenzothiazolyl-6-dimethyltriazene in 300 ml of p-xylene and 45 ml of glacial acetic acid was heated at 100-115° for 20 hours, after which the xylene solution was washed 3 times with water, the xylene removed by steam-distillation, and the tarry precipitate dissolved in chloroform and then treated as indicated above. Yield 3.7 g (29 %). It was found that the xylene contains a considerable amount of 2-methylbenzothiazole, for which reason it was fractionally distilled through a column. The residue in the flask was an oily liquid, which was dissolved in dilute hydrochloric acid (1 : 1), and the solution extracted with benzene, boiled with animal charcoal, and neutralized with alkali. The deposited oil was extracted with ether, the ether was distilled off, and the residue was distilled. B. p. 237-238°, yield 1.2 g (15 %). Picrate, m.p. 153°. The mixed melting point with the picrate of authentic 2-methylbenzothiazole (m.p. 153°) was not depressed. The base readily forms a quaternary salt, and the latter forms the thiocarbocyanine with an absorption maximum at 558 mμ. Consequently, the oil isolated from the xylene (1.2 g) proved to be 2-methylbenzothiazole.

2-Methyl-6-mesitylbenzothiazole (IV). A solution of 11 g of 2-methylbenzothiazolyl-6-dimethyltriazene in 250 ml of mesitylene and 45 ml of glacial acetic acid was heated at 85-90° for 4 hours, and then at 100° for 20 hours. The mesitylene was steam-distilled, and the residue was dissolved in chloroform and chromatographed on aluminum oxide. Five grams of base was obtained as a thick oil, which was dissolved in 60 ml of strong hydrochloric acid with heating. After cooling, the solution was treated with benzene to extract any residual mesitylene and other impurities. The benzene was separated, the hydrochloric acid solution was neutralized with ammonia, and the deposited oil was extracted with benzene and chromatographed on aluminum oxide. The benzene was distilled from the eluate, leaving a thick colorless oil (3.5 g) as residue, which partially crystallized on standing. A small amount of methyl alcohol was added to the mass with stirring, and the precipitate was filtered and recrystallized from methanol. Colorless needles, yield 1.7 g (12 %).

Found %: S 11.83, 11.81. $C_{17}H_{17}NS$. Calculated %: S 11.98.

The alcoholic mother liquors were treated with a hot picric acid solution. The deposited picrate was separated and recrystallized from alcohol. Yellow needles.

Found %: N 11.35, 11.40. $C_{23}H_{20}O_7N_4S$. Calculated %: N 11.29.

We isolated 1.9 g (25 %) of 2-methylbenzothiazole from the mesitylene.

2-Methylmercapto-6-p-dimethoxyphenylbenzothiazole (IX). A solution of 12.6 g of 2-methylmercaptobenzothiazolyl-6-dimethyltriazene in 250 g of hydroquinone dimethyl ether and 50 ml of glacial acetic acid was heated in a flask with reflux condenser, and immersed in a glycerine bath, at 107-110° for 15 hours. The base was separated from the hydroquinone dimethyl ether by dissolving in hot strong hydrochloric acid, the same as indicated above. The hydrochloric acid filtrates were combined and neutralized with 20 % sodium hydroxide solution. The deposited oil was extracted with chloroform, and the solution was chromatographed twice on aluminum

oxide. The base was eluted with benzene, the benzene was distilled off, and the residue, weighing 12.4 g, was obtained as a light-yellow oil. The oil was dissolved in 50 ml of strong hydrochloric acid, and after standing for 7 hours the deposited hydroquinone dimethyl ether (0.8 g) was filtered. The hydrochloric acid solution was neutralized with ammonia, and the deposited oil crystallized the next day. The precipitate was filtered, washed with water, and dried. Yield 11.4 g (72 %). Recrystallization from methanol gave the compound as white scales. Yield 9 g. The picrate was obtained as yellow plates (from alcohol).

Found %: N 10.05, 9.99. $C_{22}H_{18}O_9N_4S_2$. Calculated %: N 10.25.

2-Methylmercapto-6-p-xylylbenzothiazole (X). A solution of 6.3 g of 2-methylmercaptobenzothiazolyl-6--dimethyltriazene in 100 ml of p-xylene and 20 ml of glacial acetic acid was heated at 100° for 15 hours. At the end of heating the p-xylene was steam-distilled, and the tarry mass was dissolved in benzene and chromatographed twice on aluminum oxide. A thick yellow oil was obtained, which could not be made to crystallize. Yield 2.65 g (32.7 %). The picrate was obtained as yellow prisms (from alcohol).

Found %: N 10.64, 10.53. $C_{22}H_{18}O_7N_4S_2$. Calculated %: N 10.89.

2-Methylmercapto-6-mesitylbenzothiazole (XI). A solution of 12.6 g of 2-methylmercaptobenzothiazolyl--6-dimethyltriazene in 130 ml of mesitylene and 50 ml of glacial acetic acid was heated at 90° for 4 hours, and then at 100-105° for 20 hours. The mesitylene was steam-distilled, and the tarry mass was dissolved in chloroform and chromatographed twice on aluminum oxide. The base was eluted with benzene. Six grams of thick yellow oil wereobtained. It was dissolved in 60 ml of hydrochloric acid, the solution extracted with benzene, and the hydrochloric acid solution separated and neutralized with 20 % sodium hydroxide solution. An oil was obtained that crystallized the next day. The precipitate was filtered and washed with water and several drops of methanol. Yield 2.2 g (14.7 %). The picrate was obtained as tiny yellow tablets (from alcohol).

Found %: N 10.66, 10.69. $C_{23}H_{20}O_7N_4S_2$. Calculated %: N 10.60.

2-Methyl-5-p-dichlorophenylbenzothiazole (V). To a melt of 250 g of p-dichlorobenzene in a flask was added 11 g of 2-methylbenzothiazolyl-5-dimethyltriazene, and then 50 ml of glacial acetic acid. The mixture was heated at 107-110° for 15 hours. The molten mass was then treated with 130 ml of strong hydrochloric acid, the mixture boiled, and then cooled rapidly. The deposited p-dichlorobenzene wasfiltered. The indicated operation was repeated twice. The hydrochloric acid solution was neutralized with sodium hydroxide, and the obtained brown precipitate was separated, dried in the air, dissolved in chloroform, and chromatographed twice on aluminum oxide. Removal of the solvent from the eluate gave a light-yellow oil, which crystallized after stirring with 10 ml of alcohol. The crystals weighed 5.2 g, m.p. 90-93°. Recrystallization from methanol gave 3.9 g (26.5%) of colorless needles , m.p. 110-111°.

Found %: Cl 23.90, 23.91. $C_{14}H_9NSCl_2$. Calculated %: Cl 24.14.

The picrate was obtained as lustrous yellow needles.

Found %: N 10.55, 10.45. $C_{20}H_{12}O_7N_4SCl_2$. Calculated %: N 10.70.

2-Methyl-5-p-dimethoxyphenylbenzothiazole (VI). To a melt of 250 g of hydroquinone dimethyl ether in a flask was added 11 g of 2-methylbenzothiazolyl-5-dimethyltriazene and 50 ml of glacial acetic acid. The mixture was heated at 95-110° for 15 hours. Then the molten mass was boiled 4 times with 120 ml portions of concentrated hydrochloric acid. The hydrochloric acid solution was neutralized with 20 % sodium hydroxide, the thick brown oil was extracted with benzene, and the solution was chromatographed on aluminum oxide. A light-yellow oil was obtained (4.2 g), which was dissolved in 45 ml of strong hydrochloric acid, the solution cooled, and the deposited hydroquinone dimethyl ether filtered. The hydrochloric acid solution was neutralized with ammonia, and the light-yellow oil that separated here became crystalline. Recrystallization from benzine gave the compound as colorless crystals. Yield 3.22 g (22.6 %).

The picrate was obtained as light-yellow prisms (from alcohol).

Found %: N 10.83, 10.73. $C_{22}H_{18}O_9N_4S$. Calculated %: N 10.89.

2-Methyl-5-p-xylylbenzothiazole (VII). To a solution of 11 g of 2-methylbenzothiazolyl-5-dimethyltriazene in 350 ml of pure p-xylene was added 50 ml of glacial acetic acid. The mixture was heated at 100-105° for 20 hours. The p-xylene was steam-distilled, and the tarry residue was dried, dissolved in benzene with the addition of a small amount of chloroform, and chromatographed on aluminum oxide. The base was eluted with

benzene and chromatographed a second time. A thick, colorless oil was obtained, which crystallized on standing. Yield 4 g (31 %).

The picrate was obtained as yellow prisms (from methanol).

Found %: N 11.45, 11.53. $C_{22}H_{18}O_7N_4S$. Calculated %: N 11.61.

2-Methyl-5-mesitylbenzothiazole (VIII). A solution of 5.5 g of 2-methylbenzothiazolyl-5-dimethyltriazene in 130 ml of mesitylene and 25 ml of glacial acetic acid was heated at 90° for 4 hours, and then at 100-105° for 20 hours. After distilling off the mesitylene the tarry residue was dissolved in chloroform and chromatographed on aluminum oxide. The benzene was distilled from the eluate, the residual light-yellow oil (2.24 g) was dissolved in 5 ml of alcohol, and to the hot solution was added 1.7 g of picric acid in 10 ml of alcohol. The mixture was boiled for 10 minutes, cooled, and the picrate filtered, washed with 10 ml of alcohol, and then with 10 ml of ether. Weight 2.5 g, m.p. 175-176°. A suspension of 2.2 g of the picrate of 2-methyl-5-mesitylbenzothiazole in 70 ml of water was heated to the boil. Then a solution of 1.5 g of sodium acetate in 10 ml of water was added. The deposited oil was extracted with ether, the extract dried over potash, the ether distilled off, the residual light-yellow oil dissolved in 7 ml of strong hydrochloric acid, and the solution washed with benzene and then neutralized with 2 % sodium hydroxide. The oil that separated here crystallized the next day. The precipitate was filtered and recrystallized from alcohol. Yield 0.95 g (14.2%).

Found %: S 12.05, 12.26. $C_{17}H_{17}NS$. Calculated %: S 11.98.

The picrate was obtained as yellow plates (from alcohol).

Found %: N 11.30, 11.12. $C_{23}H_{20}O_7N_4S$. Calculated %: N. 11.29.

SUMMARY

1. The synthesis of several benzothiazolyldimethyltriazenes was described.

2. The reaction of benzothiazolyldimethyltriazenes with p-disubstituted derivatives of benzene or with mesitylene in the presence of glacial acetic acid gave 11 new arylbenzothiazoles.

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PREPARATION OF AZOMETHINE DERIVATIVES OF ARYLSULFONAMIDES

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The present work was started with the purpose of studying the reaction of N-dichlorosulfonamides with aromatic aldehydes. The halosulfonamides, being reactive and readily available substances, have attracted considerable interest on the part of chemists. They have been the subject of many investigations and at the present time, due to their oxidizing and halogenation properties, they have found considerable use as oxidizing agents [1], halogenation agents [2] and bactericidal agents [3].

To study the reaction we took N-dichlorobenzenesulfonamide and the three aldehydes: benzaldehyde, m-nitrobenzaldehyde and p-dimethylaminobenzaldehyde. It was found that the main reaction products of N-dichloroarylsulfonamides with aldehydes of the aromatic series in the presence of aluminum chloride in benzene solution are the azomethine derivatives of the arylsulfonamides, having the general formula $ArSO_2N{=}CHAr'$. It can be postulated that the reaction proceeds by the following scheme

$$ArSO_2NCl_2 + 2C_6H_6 \longrightarrow ArSO_2NH_2 + 2C_6H_5Cl \quad (1)$$

$$ArSO_2NH_2 + Ar'C\langle{}^{O}_{H} \longrightarrow ArSO_2N{=}CHAr' + H_2O \quad (2)$$

$$AlCl_3 + H_2O \longrightarrow HCl + AlCl_2OH \quad (3)$$

If the postulation that an arylsulfonamide is formed as the intermediate product is valid, then arylsulfonamides should react with aromatic aldehydes in the presence of aluminum chloride to yield the same azomethine derivatives. The validity of this postulation was confirmed experimentally.

From the literature data on the reaction of arylsulfonamides with aldehydes it is known that this reaction has been studied by many authors, but individual substances have been isolated only in the reaction of arylsulfonamides with formaldehyde. In 1893 Magnus-Levy [4] isolated in the reaction of benzenesulfonamide with formaldehyde a product having the composition $(C_7H_7SO_2N)_2$, and later Hugg [5] obtained from p-toluenesulfonamide and formaldehyde the hydroxymethylamide $p\text{-}CH_3C_6H_4SO_2NHCH_2OH$. In other cases the formation of mixtures is indicated, used as plasticizers, tanning agents and synthetic resins, as is evidenced by a number of published patents [6]. Toward the end of 1955, at about the time that the present work was concluded, a paper was published by Lichtenberger, Fleury and Barette [7], in which the condensation of aldehydes with arylsulfonamides was studied. They described some of the compounds that had also been obtained by us.

Azomethine compounds, i.e. Schiff bases, are obtained at the present time by the condensation of aldehydes with amines, and have been studied with the purpose in mind of using them as dyes. The preparation of this class of compounds and their properties have been studied in detail [8 - 11]. Azomethine compounds, as intermediate products, are used in practice for the synthesis of various compounds, in particular of secondary amines, o-nitrobenzaldehyde, 1-aminoanthraquinone-2-carboxaldehyde [12] and 1,4-diaminoanthraquinone-2-carboxaldehyde [13], and in the synthesis of unsymmetrical diaminodiphenylmethane bases [14]. As a result, compounds of the azomethine series represent both practical and theoretical interest.

We studied the preparation and properties of the azomethine derivatives of benzenesulfonamide and p-chlorobenzenesulfonamide obtained by reaction with the aldehydes – benzaldehyde, m-nitrobenzaldehyde, p-dimethylaminobenzaldehyde and furfural. The obtained azomethine derivatives $ArSO_2N{=}CHAr'$ represent crystalline substances, readily soluble in benzene, dioxan , hot petroleum ether and hot alcohol, and insoluble in carbon tetra-

chloride and water. Some of them are colored yellow and some are colored orange. The obtained compounds are listed in the table.

Azomethine Derivatives of Arylsulfonamides $ArSO_2N=CHAr'$

Substance Nos.	Ar	Ar'	Melting point
(I)	C_6H_5	C_6H_5	81—82°
(II)	C_6H_5	m-$NO_2C_6H_4$	122—124
(III)	C_6H_5	n-$(CH_3)_2NC_6H_4$	194—195
(IV)	C_6H_5	C_4H_3O	126—127
(V)	n-ClC_6H_4	C_6H_5	104—106
(VI)	n-ClC_6H_4	m-$NO_2C_6H_4$	159—160
(VII)	n-ClC_6H_4	n-$(CH_3)_2NC_6H_4$	150—152
(VIII)	n-ClC_6H_4	C_4H_3O	101—102

A study of some of the properties of these substances confirms the structure assigned to them. When heated in water solutions, and some even in the cold, they suffer hydrolysis with the formation of the starting arylsulfonamides and aldehydes. N-benzalbenzenesulfonamide is hydrolyzed with especial ease.

$$ArSO_2N=CHAr' + HOH \longrightarrow ArSO_2NH_2 + Ar'CHO$$

EXPERIMENTAL

Reaction of Dichloroamine With Benzaldehyde. A mixture of 0.1 mole of aluminum chloride (13.3 g) and 150 ml of benzene was placed in a three-necked flask, fitted with stirrer and reflux condenser with outlet tube. The outlet tube was connected to an absorption flask, containing 150 ml of water to trap the evolved hydrogen chloride. A solution of 0.1 mole of chloramine-B (22.2 g) in 50 ml of benzene was added to the mixture in drops. If well-dried substances were taken for reaction, then hardly any hydrogen chloride was evolved. The mixture was cooled with ice water. The chloramine was added at such a rate that the temperature of the mixture did not exceed 25-30°. Toward the end of reaction all of the aluminum chloride went into solution.

To the obtained solution was added in small portions 0.2 mole of benzaldehyde (21.3 g). Hydrogen chloride was evolved during the time of adding the benzaldehyde. The reaction mixture was heated for 5 hours on the water bath. At the end of reaction 10 ml of formic acid was added to the flask. After 40-60 minutes a precipitate of aluminum salts deposited, which was separated and washed with benzene.

The benzene was vacuum-distilled from the solution, after which the N-benzalbenzenesulfonamide (I) deposited as well-formed crystals. The filtrate was separated, and the precipitate was dried and recrystallized from petroleum ether. The chlorobenzene was removed from the mother liquor by distillation through a column at 120-140° (10 mm). The residue, representing benzalbenzenesulfonamide, was added to that obtained earlier. To identify it the chlorobenzene was redistilled, collecting the fraction with b.p. 131-133° (760 mm). The yield of chlorobenzene was 7.5 g (67 %). The total yield of (I) was 47 %, m.p. 80-82°.

Found %: N 5.61, 5.68. M 267.9, 240.0. $C_{13}H_{11}O_2NS$. Calculated %: N 5.71. M 245.25.

Titration of the solution contained in the absorption flask gave 0.137 mole of hydrogen chloride.

N-Benzalbenzenesulfonamide is a colorless crystalline substance, suffering decomposition when allowed to stand in the air with the formation of benzenesulfonamide.

Cleavage of N-benzalbenzenesulfonamide (I) with Water. A mixture of 0.98 g of (I) and 30 ml of water was heated on a boiling water bath for 2 hours and then allowed to stand for a day. The obtained precipitate was separated and washed with hot petroleum ether. The benzenesulfonamide, insoluble in petroleum ether, was recrystallized from benzene, and failed to depress the melting point when mixed with authentic benzenesulfonamide; yield 62.5 %.

Reaction of Dichloroamine With m-Nitrobenzaldehyde and With p-Dimethylaminobenzaldehyde. The reaction was run in the same manner as described above. The reaction mixture was heated for 10 hours on the water bath. In the case of the m-nitrobenzaldehyde the benzene solution on cooling gave a precipitate of well-formed crystals of m-nitrobenzalbenzenesulfonamide (II). The benzene was vacuum-distilled from the mother liquor, and the resulting precipitate of (II) was added to that obtained earlier.

In the case of the p-dimethylaminobenzaldehyde only apart of the p-dimethylaminobenzalbenzenesulfonamide (III) deposited when the benzene solution was cooled. A second portion deposited together with aluminum salts from the hot benzene solution. (III) was extracted from the mixture with acetone, the acetone was vacuum-distilled, and the residue was added to the earlier obtained substance. The benzene was vacuum-distilled from the mother liquor, and the chlorobenzene was collected by distillation through a column at 100-104° (10 mm). The yield of chlorobenzene was 74.8 %. In both cases about 0.8 mole of hydrogen chloride was evolved.

N-m-Nitrobenzalbenzenesulfonamide (II), yield 58.2 %, m.p. 119-122° (from a 1 : 1 mixture of petroleum ether and benzene), colorless crystals.

Found %: N 9.7, 9.59. M 281.0, 300.0. $C_{13}H_{10}O_4N_2S$. Calcualted %: N 9.65. M 290.23.

N-p-Dimethylaminobenzalbenzenesulfonamide (III), yield 52.5 %, m.p. 192-195° (from benzene). Orange crystals.

Found %: N 9.48, 9.29. $C_{15}H_{16}O_2N_2S$. Calculated %: N 9.79.

Reaction of Arylsulfonamides With Benzaldehyde. A mixture of 0.025 mole of aluminum chloride and 30 ml of benzene was charged into a three-necked flask, fitted with stirrer and reflux condenser with outlet tube. The outlet tube was connected to an absorption flask, containing 150 ml of water to trap the evolved hydrogen chloride. To the mixture was added 0.025 mole of the arylsulfonamide (benzenesulfonamide 3.9 g, p-chlorobenzenesulfonamide 4.8 g) in small portions. To the obtained solution was then added a solution of 0.025 mole of benzaldehyde (2.7 g) in drops. The mixture was heated for 5 hours. At the end of reaction an oil settled on the bottom of the reaction flask. The benzene solution was decanted and the benzene was vacuum-distilled; the finely crystalline residue of benzalarylsulfonamide was recrystallized from petroleum ether. The amount of HCl evolved was 92.5 % of the theoretical (based on equation 3). The yield of N-benzalbenzenesulfonamide was 44%, m.p. 80-82°. Its mixed melting point with the N-benzalbenzenesulfonamide obtained earlier was not depressed. The yield of N-benzal-p-chlorobenzenesulfonamide was 65.5 %.

Found %: N 5.01, 5.25. M 261.70, 284.50. $C_{13}H_{10}O_2NClS$. Calculated %: N 5.02. M 279.71.

The Reaction of Arylsulfonamides With m-Nitrobenzaldehyde was run in the same manner as described above for benzaldehyde. At the end of reaction a precipitate was obtained, which was separated from the hot solution. Cooling of the mother liquor gave a precipitate of N-m-nitrobenzalarylsulfonamide (II), yield 60.2 %, m.p. 122-124°; its mixed melting point with the (II) obtained in the reaction of m-nitrobenzaldehyde with chloramine was not depressed. The yield of N-m-nitrobenzal-p-chlorobenzenesulfonamide was 74 %.

Found %: N 8.76, 8.90. M 323.60, 314.10. $C_{13}H_9O_4N_2ClS$. Calculated %: N 8.62. M 324.68.

The Reaction of Arylsulfonamides With p-Dimethylaminobenzaldehyde was run in the same manner as described above for benzaldehyde. At the end of reaction the obtained precipitate was separated from the hot solution. A small amount of N-p-dimethylaminobenzalarylsulonamide was obtained as a precipitate when the solution was cooled. The remainder of the product was extracted with hot benzene from the precipitate that had deposited from the reaction mixture. Yield of N-p-dimethylaminobenzalbenzenesulfonamide (III) 60.5 %, m.p. 194-195°, which agrees with the melting point of the product obtained from the chloramine and p-dimethylaminobenzaldehyde.

The yield of N-m-dimethylaminobenzal-p-chlorobenzenesulfonamide (VII) was 50 %.

Found %: N 8.25, 8.73. $C_{15}H_{15}O_2ClN_2S$. Calculated %: N 8.67.

The Reaction of Arylsulfonamides With Furfural was run in the same manner as described above. The reaction mixture was heated with good stirring for 2 hours, in which connection it became very dark. At the end of reaction the hot mother liquor was decanted from the oil that had settled on the bottom of the flask. Cooling of the mother liquor gave the p-furfuralarylsulfonamide as a precipitate. To obtain more complete separation of the product the benzene was vacuum-distilled from the mother liquor, and the residue was added to the earlier

obtained N-fururalarylsulfonamide. The product was dried in a desiccator and recrystallized from petroleum ether.

The yield of N-furfuralbenzenesulfonamide (IV) was 51.3 %. Slightly yellowish crystals from petroleum ether.

Found %: N 6.29, 6.22, M 233.4, 233.1. $C_{11}H_9O_3NS$. Calculated %: N 6.60. M 235.2.

The yield of N-furfural-p-chlorobenzenesulfonamide (VIII) was 52.1 %. Slightly yellowish prisms.

Found %: N 5.72, 5.56. M 259.0, 267.8. $C_{11}H_8O_3NClS$. Calculated %: N 5.39. M 269.66.

The furfuralarylsulfonamides are crystalline, slightly yellow-colored substances, readily soluble in cold acetone and dioxan , somewhat more difficultly soluble in cold benzene, soluble in hot petroleum ether and in alcohol, and insoluble in water.

SUMMARY

1. A scheme was proposed for the reaction of N-dichloroarylsulfonamides with aromatic aldehydes.

2. The reaction of arylsulfonamides with aromatic aldehydes in the presence of aluminum chloride was studied.

3. Eight new azomethine derivatives of arylsulfonamides were obtained and characterized.

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THE MOBILITY OF THE FLUORINE IONS OF FLUOSILICATES AS A FUNCTION OF THE RADII OF THE CATIONS

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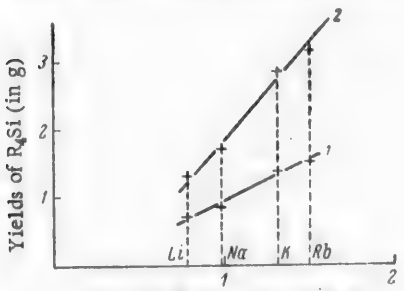
The mobility of the fluorine ions in fluosilicate molecules is closely associated with their ability to react with mixed organomagnesium compounds. We had established [1] that the yields of tetrasubstituted monosilanes formed in such reactions, at least in the reaction of the fluosilicates of lithium, sodium, potassium and rubidium with either ethylmagnesium bromide or benzylmagnesium chloride, and also in the reaction of the latter compounds with the analogous salts of calcium, strontium and barium, show a nearly linear relationship to the radii of the cations with the same valence. It should be mentioned that it was experimentally shown by E. M. Soshestvenskaya [2], who studied the reaction of benzylmagnesium chloride with sodium fluosilicate under various conditions, that neither increasing the time of heating above 1 hour nor raising the reaction temperature from 160-170° to 213-239° proved to have substantial influence on the yields of tetrabenzylmonosilane. However, it is necessary to consider the influence of raising the temperature when the reaction is run with the fluosilicates of potassium and rubidium, since in this case the reaction readily becomes violent due to the strong evolution of heat. From this it follows that a necessary condition for the above-mentioned rule to be valid is to have a nearly constant temperature regime.



Yields of tetrasubstituted monosilanes as a function of the radii of the cations in the reaction of the fluosilicates of lithium, sodium, potassium and rubidium with n-propylmagnesium bromide and n-butylmagnesium bromide.
1) tetra-n-propylmonosilane, 2) tetra-n-butylmonosilane.

As became clear from the results of our later experiments (see Fig.), the found rule is also valid for the reaction of the fluosilicates of lithium, sodium, potassium and rubidium with n-propylmagnesium bromide and n-butylmagnesium bromide. The same as in the similar experiments described earlier, the nature of the organic radical of the mixed organomagnesium compound also exerts considerable influence on the yield of the tetrasubstituted monosilane.

EXPERIMENTAL

Preparation of Starting Products

A solution of n-propylmagnesium bromide was prepared from 58 g of n-propyl bromide, 11.5 g of magnesium and 168 ml of absolute ether. The yield of n-propylmagnesium bromide was 95 %. For each experiment we took 35.1 ml portions of the solution, each portion containing 11.90 g of n-propylmagnesium bromide.

A solution of n-butylmagnesium bromide was prepared from 50.4 g of n-butyl bromide, 9 g of magnesium and 130 ml of absolute ether. The yield of n-butylmagnesium bromide was 89.1 %. For each experiment we took 38.2 ml of this solution, each portion containing 13.03 g of n-butylmagnesium bromide.

The fluosilicates were thoroughly ground, sifted through a screen, and dried in a vacuum-desiccator over sulfuric acid.

All of the experiments were run in similar-sized Erlenmeyer flasks.

Reaction of n-Propylmagnesium Bromide With Lithium Fluosilicate. To 3.12 g of lithium fluosilicate was added a portion of the Grignard reagent, then the ether was distilled off on the water bath, and finally the residue was heated for an hour in an oil bath (160-170°). By sufficiently deep immersion of the flask in the oil it was possible to keep the difference in the temperature inside the flask and in the bath to a minimum. The formation of a white fog became very pronounced when the temperature inside the flask reached 149°. At this point the bath was immediately removed and a stream of air was used to cool the flask externally. However, despite this the temperature of the reaction mixture rose to 174° in 1 minute. On conclusion of reaction the flask was cooled with ice water, and the mixture was diluted with ether up to the original volume. Then with continued cooling the reaction product was very cautiously decomposed with 25 ml of 14 % hydrochloric acid (accompanied by the evolution of propane), the ether layer separated from the water layer, the water layer extracted twice with diethyl ether (in 10 ml portions), the ether solutions combined and dried over calcium chloride, and finally the ether was removed by distillation on the water bath. The residual liquid, after adding to it a small amount of similar product that had been isolated in the redistillation of the removed ether, was fractionally distilled twice at atmospheric pressure. From 1.06 g of this liquid we isolated 0.18 g of a fraction with b.p. up to 190°, and 0.73 g of a substance that distilled mainly at 207-212° and proved to be tetra-n-propylmonosilane [3].

Found %: C 72.01; H 14.29. $C_{12}H_{28}Si$. Calculated %: C 71.89; H 14.09.

Reaction of n-Propylmagnesium Bromide With the Fluosilicates of Sodium, Potassium and Rubidium. The amounts of sodium, potassium and rubidium fluosilicates taken for experiment were 3.76, 4.41 and 6.26 g, respectively. The time and temperature of heating were kept the same as in the preceding experiment. However, the behavior of these salts proved to be different. In the reaction with the sodium salt a violent reaction, accompanied by self-heating and the appearance of a copious white fog, began when the temperature inside the flask reached 152° (in 3 minutes the temperature rose to 191°). In the experiment with the potassium salt a sharp rise in the temperature began at 147°, and in 3 minutes, despite external cooling, it rose to 215°. In the experiment with the rubidium salt a spontaneous rise in the temperature began at 144°; by resorting to cooling it proved possible to keep the reaction within the desired temperature limits. The products of all three reactions were worked up in the same manner as in the experiment with lithium fluosilicate. The decomposition of the reaction products with hydrochloric acid went violently in the case of the sodium salt, and was somewhat calmer in the other two cases. The yields of crude substance, remaining after removal of the ether, were respectively 1.19, 1.51 and 1.82 g. After two distillations in each case we respectively isolated 0.19, 0.17 and 0.19 g of fractions with b.p. up to 190°, and also 0.86, 1.36 and 1.52 g, respectively, of fractions with b.p. 207-212°, consisting of tetra-n--propylmonosilane. All of the fractions with b.p. up to 190° were combined and fractionally distilled, in which connection we obtained 0.51 g of a colorless liquid with b.p. 67-71°, which proved to be n-hexane.

Found %: C 83.57; H 16.44. C_6H_{14}. Calculated %: C 83.61; H 16.39.

Reaction of n-Butylmagnesium Bromide With Lithium Fluosilicate. To 3.12 g of lithium fluosilicate was added a portion of the n-butylmagnesium bromide solution, the ether was removed by distillation on the water bath, and the residue was heated in an oil bath at 160-170° for 1 hour. The reaction proceeded calmly, without a spontaneous temperature rise inside the flask. All of the ether that had been distilled off was returned to the reaction product after cooling, and then the reaction product was cautiously decomposed by the addition of 25 ml of 14 % hydrochloric acid with cooling, after which the water layer was separated and extracted twice with ether (10 ml portions), followed by the drying of the combined ether solution over calcium chloride, and finally, removal of the ether by distillation. The liquid residue (2.10 g), after adding to it the residue obtained in the fractional distillation of the distilled ether, was fractionally distilled twice to give 0.37 g of a fraction with b.p. 118-124° and 1.32 g of a liquid residue, which proved to be tetra-n-butylmonosilane [4].

Found %: C 75.11; H 14.27. $C_{16}H_{36}Si$. Calculated %: C 74.89; H 14.15.

Reaction of n-Butylmagnesium Bromide With Sodium, Potassium and Rubidium Fluosilicates. The sodium, potassium and rubidium fluosilicates were taken in the same amounts as in the above-described experiments with n-propylmagnesium bromide. The time and temperature of heating were also kept the same. In the experiment with the sodium salt a definitely exothermic process began when the oil bath was heated to 151°, and despite the

cessation of heating the temperature of the reaction mixture rose to 172° in 4 minutes. In the experiments with the potassium and rubidium salts the evolution of heat began when the temperature inside the flask reached 149° and 113°, respectively. The exothermic heat was accompanied by the copious evolution of a white fog. Despite removal of the bath and cooling with a stream of air, in the experiment with the potassium salt the temperature rose to 175° in 1 minute, while in the experiment with the rubidium salt the temperature remained for 36 minutes at a level that exceeded the bath temperature by 10-21°. In the experiment with the sodium salt the amount of heat evolved when the reaction product was decomposed with hydrochloric acid was less than in the case of the lithium salt, it proved to be even less in the experiment with the potassium salt, and was minimum in the experiment with the rubidium salt. The products, remaining after removal of the ether by distillation (2.25, 3.59 and 4.08 g, respectively), gave as the end result of fractional distillation respectively 0.57, 0.29 and 0.42 g of fractions with b.p. 118-124°, and in addition, 1.70, 2.85 and 3.15 g of undistilled liquid, which proved to be tetra-n--butylmonosilane, The fractions, distilling at 117-123°, were combined and redistilled to give 1.32 g of a liquid with b.p. 122-124°, which proved to be n-octane.

SUMMARY

1. A comparative study was made of the reaction of the fluosilicates of lithium, sodium, potassium and rubidium with n-propylmagnesium bromide and n-butylmagnesium bromide.

2. It was established that the yields of the tetrasubstituted monosilanes, the same as in the earlier studied cases, show a linear relationship to the values of the radii of the fluosilicate cations.

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HALOARYLATION OF UNSATURATED COMPOUNDS WITH AROMATIC DIAZO COMPOUNDS

V. CHLOROARYLATION OF DIVINYL. SYNTHESIS OF α-ARYLBUTADIENES

A. V. Dombrovsky and A. P. Terentyev

It had been shown by us [1] that in aqueous acetone solution, in the presence of cupric chloride with the addition of calcium hydroxide, divinyl reacts with phenyldiazonium chloride, giving 4-chloro-1-phenyl-2-butene in good yield. In this paper we communicate the results of studying the chloroarylation of divinyl with other diazotized aromatic amines. The chloroarylbutenes obtained in this manner (compounds I - XII, Table 1) were then converted by the method developed by us [2] into α-arylbutadienes.

The reaction between divinyl and compounds of type $Ar-N_2-Cl$, containing positive substituents (CH_3-, CH_3O- groups) in the benzene ring, has not been realized up to now. It was found that divinyl reacts with diazotized toluidines and p-anisidine in a medium with pH 4-5, regulated by the additions of $Ca(OH)_2$. In this reaction the aryl radical and chlorine atom of the diazonium salt add to divinyl in the 1,4 position.

$$CH_2=CH-CH=CH_2 + Ar-N_2Cl \rightarrow Ar-CH_2-CH=CH-CH_2Cl + N_2$$

Divinyl reacts in a similar manner with the p-chloro-, p-bromo-, 2,4-dichloro-, 2,4-dibromo- and p-iodophenyldiazonium salts. The reaction between divinyl and $BrC_6H_4-N_2-Cl$ in the presence of $Ca(OH)_2$ proceeds vigorously, but together with halo derivative (VII), a substantial amound of α-p-bromophenylbutadiene (XIX) is formed, which suffers polymerization during reaction with a substantial reduction in the total yield. When the reaction is run in acid medium the yield of (VII) is low. Better yields of (VII) are obtained if the reaction is run in the presence of sodium acetate, but in this case also the crude reaction product contains about 10 % of (XIX). The reaction of divinyl with a solution of the prepared dry salt $p\text{-}IC_6H_4-N_2-Cl$ gives 4-chloro-1-(p-iodophenyl)-2-butene in about 30% yield and about 20 % of diiodobenzene.

It was established by us that in contrast to the aromatic diazonium chlorides with positive substituents of halogen atoms in the nucleus, the nitrophenyldiazonium chlorides react with divinyl in hydrochloric acid medium to give better yields than when the reaction is run in acetate buffer or in the presence of $Ca(OH)_2$. Considerable tar formation occurs in the latter two cases. All three isomers of 4-chloro-1-nitrophenyl-2-butene (X - XII) were synthesized by us in high yields.

The data on the chloroarylbutenes, obtained by the chloroarylation of divinyl, are presented in Table 1. It should be mentioned that the position of the substituent in the nucleus of the diazonium salt exerts very little influence on the yield of chloroarylation product.

The chloroarylbutenes are high-boiling liquids with a slight yellow color; the compounds, containing a NO_2 group, have a more intense yellow color. The chloroarylbutenes are extremely stable, and can be kept for a long time without noticeable change. Their structure was proved by oxidation. Reaction with $KMnO_4$ under mild conditions leads in all cases to the formation of chloroacetic acid and the corresponding arylacetic acids.

$$Ar-CH_2-CH=CH-CH_2Cl \rightarrow Ar-CH_2-COOH + CH_2Cl-COOH$$

Since the chlorine atom found in the chloroarylbutenes is of the allylic type, then undoubtedly it can be made to undergo the transformations that have been described by us for 4-chloro-1-phenyl-2-butene [1].

TABLE 1

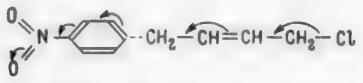
4-Chloro-1-aryl-2-butenes of General Formula $Ar-CH_2-CH=CH-CH_2Cl$. Obtained by the Chloroarylation of Divinyl

Compound Nos.	Ar	Yield in %	Constants			Analysis data						Melting point of arylacetic acid	Lit. Ref.
			boiling point	n_D^{20}	d_4^{20}	C		H		Cl			
						found	calc.	found	calc.	found	calc.		
(I)	p-$CH_3C_6H_4$	52	112—114° (at 6 мм)	1.5349	1.0227	72.90 73.08	73.12	7.60 7.65	7.25	19.52 19.65	19.63	93° (from water)	—
(II)	m-$CH_3C_6H_4$	50	107—109 (at 3 мм)	1.5354	1.0320	73.28 73.25		7.26 7.32		19.02		60 (from water)	—
(III)	o-$CH_3C_6H_4$	52.5	94—95 (at 2 мм)	1.5400	1.0434	73.16 73.11		7.19 7.18		19.64 19.30		88 (from water)	—
(IV)	p-$CH_3OC_6H_4$	40.6	124—126 (at 2 мм)	1.5450	1.0932	67.23 67.19	67.11	6.55 6.68	6.66	17.88 17.76	18.03	86 (from water)	—
(V)	p-ClC_6H_4	67	125—126 (at 2 мм)	1.5518	1.1670	60.12 60.04	59.72	5.02 4.93	5.01	35.29 35.04	35.26	155 (from water)	—
(VI)	2,4-$Cl_2C_6H_3$	64	145—148 (at 4 мм)	1.5677	1.2972	50.60 50.64	50.99	3.85 3.92	3.85	45.65 45.66	45.16	137.5 (from benzene)	—
(VII)	p-BrC_6H_4	60	117—118 (at 2 мм)	1.5728	1.4218	48.68 48.74	48.91	3.81 3.85	4.11	—	—	113 (from water)	[7]
(VIII)	2,4-$Br_2C_6H_3$	62	155—158 (at 2 мм)	1.6051	1.7095	36.90 37.36	36.99	2.81	2.79 2.87	—	—	114 (from water)	—
(IX)	p-IC_6H_4	30	137—140 (at 2 мм)	1.6082	1.5790	22.20 22.23	21.81	1.26 1.34	1.22	11.88 11.88	12.12	134 (from water)	—
(X)	p-$O_2NC_6H_4$	75	145—146 (at 2 мм)	1.5740	1.2243	56.71 56.61		4.77 4.78		16.45 16.72		150 (from water)	[3]
(XI)	m-$O_2NC_6H_4$ *	57	174—175 (at 7 мм)	1.5680	1.2188	56.76 56.66	56.73	4.89 4.83	4.76	16.43 16.26	16.75	117 (from water)	—
(XII)	o-$O_2NC_6H_4$	66	155—156 (at 3 мм)	1.5692	1.2226	56.52 56.51		4.70 4.78		16.46 16.69		137 (from alcohol)	[4]

* Found %: N 7.17, 7.14. $C_{10}H_{10}O_2NCl$. Calculated %: N 6.62.

Of special interest is the cleavage of HCl from the chloroarylbutenes for the purpose of obtaining, in most cases, the difficultly available α-arylbutadienes. The chloronitrophenylbutenes are easily converted into the corresponding α-nitrophenylbutadienes by the known method [3, 4] of heating with potassium hydroxide in methanol. However, the chloroarylbutenes with 1st order substituents or halogen atoms present in the benzene ring, the same as chlorophenylbutene [2], react in an ill-defined manner with alcoholic alkalies: a mixture of approximately equal amounts of alkoxy derivative and α-arylbutadiene is obtained. Such a difference in the behavior of the chloroarylbutenes should be explained as due to the fact that under the influence of the nitro group, found in the benzene ring, the hydrogen atom in position 1 becomes so labile that it is easily cleaved as HCl.

On the other hand, substituents in the ring with a positive inductive effect tend to reduce the lability of this H atom. Consequently in this case, together with HCl cleavage, there is nucleophilic replacement of the alkoxy group by the chlorine atom.



Attempts to cleave HCl from chloroarylbutenes with positive substitutents in the ring by means of quinoline, dimethylaniline or diethylaniline, and also by means of pyridine and triethylamine, gave negative results: for all practical purposes the reaction does not go in the cold, while if heating is employed the formed diene suffers polymerization and becomes tarry.

TABLE 2

α-Arylbutadienes of General Formula $Ar-CH=CH-CH=CH_2$, Obtained From 4-Chloro-1-aryl-2-butenes

Compound Nos.	Ar	Yield (in %)	Constants: temperature b.p.	Constants: temperature m.p.	Constants: n_D^{20}	Constants: d_4^{20}	Melting point of adduct with maleic anhydride	Literature references
(XIII)	p-$CH_3C_6H_4$	91	90—91° (at 9 мм)	26°	1.5970*	0.9079*	117°	[6]
(XIV)	m-$CH_3C_6H_4$	92	85—87 (at 7 мм)	—	1.5995	0.9212	77—78	[6]
(XV)	o-$CH_3C_6H_4$	96	86 (at 8 мм)	—	1.6001	0.9256	92—93	[6]
(XVI)	p-$CH_3OC_6H_4$	78	115—120 (at 6 мм)	45	—	—	141—42	[6]
(XVII)	p-ClC_6H_4	84	104 (at 9 мм)	18	1.6230	1.0728	107	[6]
(XVIII)**	2,4-$Cl_2C_6H_3$	90	—	54	—	—	134	—
(XIX)	p-BrC_6H_4	82	110 (at 3 мм)	29	—	—	139	[7]
(XX)***	p-IC_6H_4	88	—	60	—	—	160	—
(XXI)	p-$O_2NC_6H_4$	97	—	79	—	—	168	[3]
(XXII)****	o-$O_2NC_6H_4$	80	—	53	—	—	159	—
(XXIII)	m-$O_2NC_6H_4$	98	—	68	—	—	151.5	[4]

* At 28°.

** Found %: C 60.34, 60.32; H 4.01, 3.95; Cl 35.87, 35.72. $C_{10}H_8Cl_2$. Calculated %: C 60.33; H 4.05; Cl 35.62. Adduct of compound (XVIII) with maleic anhydride — found %: C 56.47, 56.42; H 3.27, 3.39; Cl 24.00, 23.70. $C_{14}H_{10}O_3Cl_2$. Calculated %: C 56.59; H 3.34; Cl 23.48.

*** Found %: I 49.38, 49.47. $C_{10}H_9I$. Calculated %: I 49.56. Adduct of compound (XX) with maleic anhydride — Found %: C 47.48, 47.60; H 3.14, 3.22; I 36.04, 36.12. $C_{14}H_{11}O_3I$. Calculated %: C 47.48; H 3.12; I 35.84.

**** Found %: C 68.45, 68.49; H 5.20, 5.29; N 7.91, 7.98. $C_{10}H_9O_2N$. Calculated %: C 68.55; H 5.18; N 8.00. Adduct of compound (XXII) with maleic anhydride — Found %: N 5.13, 5.02. $C_{14}H_{11}O_5N$. Calculated %: N 5.13.

To obtain the α-arylbutadienes we used in the present case the method developed by us for the synthesis of α-phenylbutadiene [2], using powdered potassium hydroxide in dioxane to cleave the HCl. When 0.1 mole of chloroarylbutene is used the reaction is finished in several minutes. The conditions are so mild that neither polymerization nor tarring occurs. Using this method we synthesized the dienes (XIII - XX) in high yield. The data are presented in Table 2. The α-arylbutadienes were characterized by reaction with maleic anhydride; the corresponding aryltetrahydrophthalic acid anhydrides were obtained.

The nuclear-substituted α-arylbutadienes are either liquids or low-melting substances. When heated or when exposed to illumination they suffer rapid polymerization. These compounds are easily oxidized in the air. Thus, the exposure of (XX) to the air for 6-8 hours results in the addition of 1 mole of oxygen.

EXPERIMENTAL

Chloroarylation of Divinyl. The chloroarylbutenes (I - VI), (VIII) and (IX) were obtained by the method described by us [1] for the synthesis of chlorophenylbutene in the presence of calcium hydroxide. In the preparation of (VII) we added sodium acetate instead of $Ca(OH)_2$ to the reaction mixture, bringing the pH of the medium up to 4.5-5.5 (an LP-4 potentiometer was used to measure the pH). To obtain (IX) we prepared the dry salt p-$IC_6H_4-N_2-Cl$ from p-iodoaniline hydrochloride and amyl nitrite by the method of [5], which when reacted with divinyl gave, in addition to (IX), 20 % of p-diiodobenzene with m.p. 127° (from methanol). Compounds (X - XII) were synthesized in the usual manner [1], but in this case alkaline agents were not added to the reaction mixture; the reaction went well at 0-8° in hydrochloric acid medium (pH 1). The yields, physicochemical constants and analytical data for the synthesized chloroarylbutenes are presented in Table 1.

Oxidation of 4-Chloro-1-aryl-2-butenes. To 0.03 mole of the chloroarylbutene with stirring and cooling (temperature of the mixture 0-2°) was added 630 ml of 2 % $KMnO_4$ solution in 18 hours. After separating the manganese dioxide the neutral products were extracted from the weakly alkaline filtrate. The filtrate was evaporated at 50-80 mm to a small volume (60-80 ml) and then acidified with dilute H_2SO_4. This resulted in the precipitation of the slightly soluble arylacetic acids. The chloroacetic acid was extracted from the acid filtrate by repeated extraction (5-6 times) with ether. The first extract, containing small amounts of $Ar-CH_2-COOH$, was discarded. After removal of the solvent the chloroacetic acid was recrystallized from petroleum ether; m.p. 56-57°. The melting points of the arylacetic acids are given in Table 1.

α-Arylbutadienes. Compounds (XII - XX) were prepared by heating the corresponding chloroarylbutenes (I - IX) with powdered potassium hydroxide in dioxan by the method of [2]. The α-nitrophenylbutadienes (XXI - XXIII) were synthesized from (X - XII) by heating with a solution of potassium hydroxide in methanol by the method of [3]. The adducts of the α-arylbutadienes with maleic anhydride were obtained in the usual manner, by heating equimolar amounts of the reactants in benzene. The obtained precipitates (at times obtained after standing for two days) were recrystallized from either ligroin or ethyl acetate. The yields, physicochemical constants and analytical data for the previously unknown compounds (both for the synthesized α-arylbutadienes and for their adducts with maleic anhydride) are presented in Table 2.

SUMMARY

1. The reaction of divinyl with a number of aryldiazonium chlorides in the presence of cupric chloride was studied. Thirteen compounds of type

$$Ar-CH_2-CH=CH-CH_2Cl,$$

were obtained, of which 8 are new compounds (Ar = o-, m- and p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, 2,4-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$, p-IC_6H_4 and m-$O_2NC_6H_4$).

2. Treatment of the synthesized chloroarylbutenes with powdered potassium hydroxide in dioxan gave in high yield a number of α-arylbutadienes, three of which (Ar = 2,4-$Cl_2C_6H_3$, p-IC_6H_4 and m-$O_2NC_6H_4$) are described for the first time.

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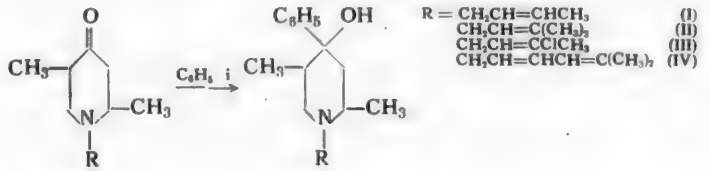
55. SYNTHETIC ANALGESIC SUBSTANCES. XVI. SYNTHESIS OF 1-ALKENYL-2,5-DIMETHYL-4-PHENYL-4-PIPERIDOLS AND THEIR PROPIONIC ESTERS. ANALOGS OF PROMEDOL AND ISOPROMEDOL. III

I. N. Nazarov and A. Sh. Sharifkanov

In recent years extensive studies have been made in our laboratory on the synthesis of esters of 4-phenyl--4-piperidols with various alkyl substituents on the nitrogen of the piperidine ring [1]. The purpose of these investigations was to study the influence of these substituents on the physiological (analgesic) activity of the propionic esters of the 2,5-dimethyl-4-phenyl-4-piperidols.

The starting 1-alkenyl- and 1-alkadienyl-2,5-dimethyl-4-phenyl-4-piperidols (I - IV) were synthesized in high yields (above 70%) by the condensation of phenyllithium with either 1-alkenyl- or 1-alkadienyl-2,5--dimethyl-4-piperidones, described in the previous communication [2].

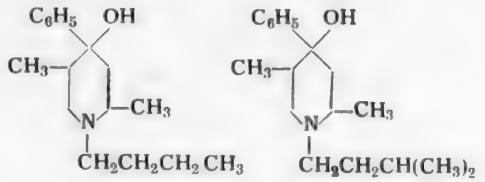


The same as in other similar reactions, the phenylpiperidols are formed here as a mixture of three stereoisomers (of the four theoretically possible), and this mixture was separated by fractional crystallization from benzine (b.p. 80-100°) into the individual compounds [3]. As a result, the following four phenylpiperidols were synthesized: 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol (I), 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4--piperidol (II), 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (III) and 1-(5-methyl-2,4-hexadienyl)--2,5-dimethyl-4-phenyl-4-piperidol (IV).

Only two stereoisomers were isolated from the mixture of isomeric 1-crotyl-2,5-dimethyl-4-phenyl-4--piperidols (I): the γ-form with m.p. 102-103° (yield 67-70% of the total amount of isolated individual forms) and the β-form with m.p. 97-98° (yield 30-33 %). Three individual stereoisomers were isolated from the mixture of isomeric 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidols (II): the γ-form with m.p. 115.5--116.5° (yield 71-80 %), the β-form with m.p. 105.5-106.5° (yield 14-25 %), and the α-form with m.p. 109.5--110.5° (yield 4-6 %). Three individual stereoisomers were also isolated from the mixture of isomeric 1-(γ--chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidols (III): the β-form with m.p. 134-135° (yield 56-58 %), the γ-form with m.p. 110-111° (yield 31-33 %), and the α-form with m.p. 132-133° (yield 9-13 % of the total amount of the isolated individual isomers). The mixture of isomeric 1-(5-methyl-2,4-hexadienyl)-2,5-dimethyl-4-phenyl--4-piperidols (IV) proved to be an oily product, and was not subjected to separation into the individual isomers.

The method of fractional crystallization from benzine does not achieve a complete separation of the above indicated phenylpiperidols into the individual isomers and substantial amounts of the substances remain as mixtures; consequently, it is impossible to make an accurate estimate of the ratios of the individual isomers.

The catalytic hydrogenation of the isolated individual stereoisomeric phenylpiperidols (I, II and III) in the presence of Raney nickel catalyst gave the corresponding stereoisomeric phenylpiperidols (V) and (VI) with saturated radicals on the nitrogen.



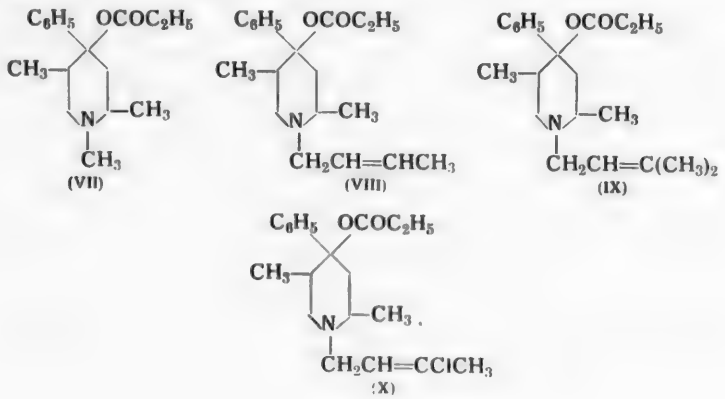
(V) (VI)

The catalytic hydrogenation of the high-melting β-isomer of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (III) with m.p. 134-135° gave the earlier described [4] low-melting β-isomer of 1-butyl-2,5-dimethyl-4-phenyl-4-piperidol (V) with m.p. 70-71°, while the hydrogenation of the low-melting γ-isomer of (III) with m.p. 110-111° gave the high-melting γ-isomer of 1-butyl-2,5-dimethyl-4-phenyl-4-piperidol (V) with m.p. 95-96°.

The hydrochloride of the propionic ester of the β-isomer of (III) with m.p. 134-135° proved to be a more active analgesic than the hydrochloride of the propionic ester of the γ-isomer with m.p. 110-111°. These facts indicate that the high-melting isomer of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 134-135° is spatially similar to the low-melting β-forms of the 1-alkyl-2,5-dimethyl-4-phenyl-4-piperidols, described in a previous communication [5].

The most suitable method for the preparation of the propionic esters of the above-described phenylpiperidols (I - III) proved to be the esterification of the latter with propionyl chloride in the presence of propionic anhydride at 115-120° for 10-11 hours. The propionyl chloride used for esterification was purified from free hydrogen chloride by distillation in the presence of 10 % diethylaniline.

To synthesize the propionic esters we used the pure β- and γ-isomers of the phenylpiperidols (I - III), being the main reaction products, while in view of their difficult availability the propionic esters of the α-isomers were not prepared. As a result, we prepared the propionic esters (VIII - X), which as the hydrochlorides were tested for their analgesic activity in the laboratory of Prof. M. D. Mashkovsky (S. Ordzhonikidze All-Union Scientific-Research Chemical-Pharmaceutical Institute).



(VII) (VIII) (IX) (X)

The analgesic activity of the obtained propionic esters (VIII - X) was compared with that of promedol, which is the hydrochloride of the propionate of the γ-isomer of 1,2,5-trimethyl-4-phenyl-4 piperidol (VII) [6]. The data on the analgesic activity of the hydrochlorides of propionic esters (VIII - X) are presented in the table.

Comparative Analgesic Activity of the γ- and β-Forms of Propionic Esters (VII - X)
[The Activity of Promedol (VII; γ-Form) Was Taken Equal to One]

	(VII)	(VIII)	(IX)	(X)
γ-Form	1	1/3	1/3	Inactive
β-Form	2-3	1	1	1/3

As a result, in all cases the β-forms show much greater analgesic activity than do the γ-isomers, as had already been mentioned earlier on the example of many other propionic esters of 1-alkyl-2,5-dimethyl-4-phenyl--4-piperidols [3, 4].

In general, all of the investigated propionic esters (VIII - X) possessed little interest as analgesics, being about 1/3 as active as promedol (VII; γ-form) and isopromedol (VII; β-form). The pharmacological properties of the compounds are most sharply impaired by the introduction of a chlorine atom in the molecule of propionic ester (X).

EXPERIMENTAL

1-Crotyl-2,5-dimethyl-4-phenyl-4-piperidol (I). The reaction was run in a three-necked 750-ml flask, fitted with mechanical stirrer, reflux condenser, dropping funnel, thermometer and a tube for nitrogen, which was passed into the mixture during the whole experiment. Into the flask was charged 110 ml of absolute ether and 5.5 g of finely cut lithium, and then a solution of 57 g of bromobenzene in 115 ml of absolute ether was added dropwise in 2 hours. Then the reaction mixture was heated for 1.5 hours at ether boil. On conclusion of reaction the flask with prepared phenylithium was cooled to -10°, and then with stirring a solution of 54.4 g of 1-crotyl-2,5--dimethyl-4-piperidone (b.p. 87-89° at 2 mm, n_D^{20} 1.4758) in 115 ml of absolute ether was added in 1.5 hours. The next day the reaction mass was heated at ether boil for 2 hours. The obtained alcoholate was hydrolyzed at 0° by the addition of 150 ml of ice water. The ether layer was separated, while the water layer was saturated with solid caustic and extracted several times with ether. The combined ether extracts were dried over sodium sulfate. Vacuum-distillation of the product gave 57.9 g (74.6 % yield) of a mixture of stereoisomeric 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidols (I) as a thick liquid with b.p. 133-135° at 2 mm, which crystallized on standing.

Fractional crystallization of the mixture from benzine (b.p. 80-110°) led to obtaining the following two individual forms of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol.

1) γ-Form with m.p. 102-103°, 10 g or 17 % of the total amount of mixed isomers.

Found %: C 79.17, 79.13; H 9.82, 9.94; N 5.37, 5.34. $C_{17}H_{25}ON$. Calculated %: C 78.72; H 9.72; N 5.39.

The Hydrochloride of the γ-Form has m.p. 138-140°.

Found %: Cl 12.18, 11.97. $C_{17}H_{26}ONCl$. Calculated %: Cl 12.60.

The catalytic hydrogenation of the γ-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol in the presence of Raney nickel catalyst in anhydrous alcohol medium gave the γ-form of 1-butyl-2,5-dimethyl-4-phenyl-4--piperidol (V) with m.p. 95-96°, which did not depress the melting point when mixed with the earlier-described specimen of this piperidol [3].

2) β-Form with m.p. 97-98°, 5 g or about 9 % of the total amount of mixed isomers.

Found %: C 78.90, 79.05; H 9.78, 9.67; N 5.39, 5.59. $C_{17}H_{25}ON$. Calculated %: C 78.72; H 9.72; N 5.39.

The Hydrochloride of the β-Form has m.p. 199-200°.

Found %: Cl 11.78, 11.78. $C_{17}H_{26}ONCl$. Calculated %: Cl 12.60.

The catalytic hydrogenation of the β-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol gave the β-form

of 1-butyl-2,5-dimethyl-4-phenyl-4-piperidol (V) with m.p. 69-70°, not depressing the melting point when mixed with the earlier obtained specimen [3].

1-(γ,γ-Dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (II). To an ether solution of phenyllithium prepared in the same manner as in the preceding experiment from 9.5 g of lithium, 129 g of bromobenzene and 350 ml of absolute ether, with ice-salt cooling was added in drops a solution of 108.5 g of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-piperidone (b.p. 84-86° at 1 mm, n_D^{20} 1.4810) in 100 ml of absolute ether in 1.5 hours. The reaction mixture was allowed to stand overnight, heated the next day at ether boil for 2 hours, and then hydrolyzed with ice water. The ether layer was separated, while the water layer was saturated with solid sodium hydroxide and then extracted with ether. The combined ether extracts were dried over sodium sulfate. After distilling off the ether the residue crystallized. Fractional crystallization of this crystalline mass from benzine led to obtaining three individual stereoisomeric forms of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (II).

1) γ-Form with m.p. 115.5-116.5°, 36 g or 27 % of the total amount of mixed isomers.

Found %: C 79.61, 79.60; H 10.10, 10.02; N 5.27, 5.23. $C_{18}H_{27}ON$. Calculated %: C 79.09; H 9.96; N 5.14.

The Hydrochloride of the γ-Form was obtained by saturating an ether solution of the free base with dry hydrogen chloride. After recrystallization from a mixture of alcohol and acetone the compound melted at 163-164°.

Found %: Cl 11.46, 11.45. $C_{18}H_{28}ONCl$. Calculated %: Cl 11.45.

The catalytic hydrogenation of this isomer (m.p. 115.5-116.5°) in the presence of Raney nickel catalyst gave the γ-isomer of 1-isoamyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) with m.p. 109-110°, obtained earlier in our laboratory [3].

2) β-Form with m.p. 105.5-106.5°, 13 g or 10 % of the total amount of mixed isomers.

Found %: C 79.60, 79.77; H 10.01, 10.04; N 5.23, 5.29. $C_{18}H_{27}ON$. Calculated %: C 79.09; H 9.96; N 5.14.

The Hydrochloride of the β-Form has m.p. 202-203° (from acetone).

Found %: Cl 11.14, 11.00. $C_{18}H_{28}ONCl$. Calculated %: Cl 11.45.

The catalytic hydrogenation of this form (m.p. 105.5-106.5°) gave the β-isomer of 1-isoamyl-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 82-83° (from benzine), synthesized earlier in our laboratory [3].

3) α-Form with m.p. 109.5-110.5°, 2 g or about 2 % of the mixed isomers.

Found %: C 79.45, 79.59; H 10.03, 10.11; N 5.25, 5.23. $C_{18}H_{27}ON$. Calculated %: C 79.9; H 9.96; N 5.14.

The Hydrochloride of the α-Form melts at 211-212° (from a mixture of alcohol and ether). Its mixture with the hydrochloride of the β-form of this piperidol (m.p. 202-203°) melted at 178-190°.

Found %: Cl 11.44, 11.67. $C_{18}H_{28}ONCl$. Calculated %: Cl 11.45.

The catalytic hydrogenation of the α-form of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 109.5-110.5°) gave the α-isomer of 1-isoamyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) with m.p. 104-105°.

Found %: N 5.25, 4.93. $C_{18}H_{29}ON$. Calculated %: N 5.08.

The mixture of this piperidol (m.p. 104-105°) with the γ-isomer of 1-isoamyl-2,5-dimethyl-4-phenyl-4-piperidol (with m.p. 109-110°) melted at 88-100°.

After isolating the individual isomers there remained 81 g of unseparated mixture.

1-(γ-Chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (III). To an ether solution of phenyllithium, prepared from 10.8 g of lithium, 111.5 g of bromobenzene and 420 ml of absolute ether, with ice-salt cooling was added in drops a solution of 127 g of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-piperidone (b.p. 111-113° at 2 mm, n_D^{20} 1.4950) in 150 ml of absolute ether in 2 hours. The reaction mass was heated for 2 hours at ether boil and then allowed to stand overnight. The next day the product was worked up in the same manner as described in the preceding experiments. The mixture of stereoisomeric 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidols, weighing 132 g, was subjected to fractional crystallization from benzine without prior vacuum-distillation. Three individual stereoisomeric forms of this piperidol were isolated as the result of the fractional crystallization.

1) γ-Form with m.p. 110-111°, 18 g or about 14 % of the total amount of mixed isomers.

Found %: C 70.14, 70.05; H 8.47, 8.41; N 4.95, 4.88; Cl 11.78. $C_{17}H_{24}ONCl$. Calculated %: C 96.44; H 8.23; N 4.76; Cl 12.07.

The Hydrochloride of the γ-Form melts at 137-139°.

Found %: Cl (Ionic) 10.89, 11.09. $C_{17}H_{25}ONCl_2$. Calculated %: Cl (Ionic) 10.74.

The catalytic hydrogenation of the γ-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 110-111°) gave the γ-form of 1-butyl-2,5-dimethyl-4-phenyl-4-piperidol (V) with m.p. 93-94°, synthesized earlier in our laboratory [3].

2) β-Form with m.p. 134-135°, 32 g or 25 % of the total amount of mixed isomers.

Found %: C 69.04, 68.95; H 7.98, 8.13; N 4.61, 4.91. $C_{17}H_{24}ONCl$. Calculated %: C 69.44; H 8.23; N 4.76.

The Hydrochloride of the β-Form has m.p. 190-191°.

Found %: Cl (Ionic) 10.86, 10.96. $C_{17}H_{25}ONCl_2$. Calculated %: Cl (Ionic) 10.74.

The catalytic hydrogenation of the β-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 134-135°) gave the β-form of 1-butyl-2,5-dimethyl-4-phenyl-4-piperidol (V) with m.p. 69-70° [3].

3) α-Form with m.p. 132-133°, 5 g or 4% of the total amount of mixed isomers.

Found %: C 70.03, 70.11; H 8.49, 8.47; N 4.62; Cl 11.61, 11.48. $C_{17}H_{24}ONCl$. Calculated %: C 69.44; H 8.23; N 4.76; Cl 12.07.

The mixture of the α-form with the β-form of this piperidol (m.p. 134-135°) melted at 115-119°.

The Hydrochloride of the α-Form has m.p. 206-207°.

Found %: Cl (Ionic) 10.98, 11.16. $C_{17}H_{25}ONCl_2$. Calculated %: Cl (Ionic) 10.74.

The mixture of this hydrochloride with the hydrochloride of the β-form of this piperidol (m.p. 190-191°) melted at 176-190°.

1-(5-Methyl-2,4-hexadienyl)-2,5-dimethyl-4-phenyl-4-piperidol (IV). To an ether solution of phenyllithium, prepared in the usual manner in a nitrogen atmosphere from 20.4 g of bromobenzene, 1.8 g of lithium and 140 ml of absolute ether, with ice-salt cooling was added in 1.5 hours a solution of 22.2 g of 1-(5-methyl-2,4-hexadienyl)--2,5-dimethyl-4-piperidone (b.p. 119-120° at 2 mm, n_D^{20} 1.5105) in 50 ml of absolute ether. On conclusion of adding the piperidone the reaction mixture was stirred for 2 hours at room temperature, and then for 2 hours at ether boil After the usual treatment the product was vacuum-distilled. We obtained 22.1 g of 1-(5-methyl-2,4--hexadienyl)-2,5-dimethyl-4-phenyl-4-piperidol as a thick oil with b.p. 160-170° at 1 mm. Yield 73 %. Repeated attempts to crystallize this product proved unsuccessful.

Found %: N 4.34, 4.70. $C_{20}H_{29}ON$. Calculated %: N 4.67.

The Hydrochloride was obtained as a noncrystallizing hygroscopic oil.

Propionate of the γ-Form of 1-Crotyl-2,5-dimethyl-4-phenyl-4-piperidol (VIII). A mixture of 2.6 g of the γ-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 102-103°), 6 ml of propionic anhydride and 2.5 ml of propionyl chloride was heated at 115-120° for 10 hours. The excess anhydride and chloride were vacuum-distilled, while the residue was treated with ether, after which it crystallized. Two recrystallizations from a mixture of acetone and alcohol (1 : 3) gave 1.55 g (44 %) of the hydrochloride of the propionate of the γ-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 169-170°.

Found %: C 68.25, 68.46; H 8.38, 8.70; N 4.23, 3.95; Cl 9.94, 10.26. $C_{20}H_{30}O_2NCl$. Calculated %: C 68.21; H 8.59; N 3.97; Cl 10.12.

Propionate of the β-Form of 1-Crotyl-2,5-dimethyl-4-phenyl-4-piperidol (VIII). A mixture of 2.6 g of the β-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 97-98°), 8 ml of propionic anhydride and 2 ml of propionyl chloride was heated at 110-115° for 6 hours. After distilling off the excess anhydride and chloride the residue was rubbed in absolute ether and then dried in a vacuum-desiccator. Weight 3 g; yield 82%. Re-

crystallization from a mixture of acetone and alcohol gave 0.6 g of the hydrochloride of the propionate of the β-form of 1-crotyl-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 181-182°.

Found %: C 68.17, 68.25; H 8.42, 8.57; N 4.35, 4.21; Cl 10.13, 10.04. $C_{20}H_{30}O_2NCl$. Calculated %: C 68.21; H 8.59; N 3.97; Cl 10.10.

The mixture of this hydrochloride with the hydrochloride of the starting piperidol (m.p. 195-196°) melted at 157-163°.

Propionate of the γ-Form of 1-(γ,γ-Dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (IX). a) A mixture of 4 g of the γ-isomer of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 115.5-116.5°), 3.5 ml of propionyl chloride, 10 ml of dry benzene and 0.3 g of magnesium turnings was vigorously stirred at 90--100° for 11 hours. At the end of heating the excess propionyl chloride and benzene were vacuum-distilled, while the residue was dissolved in 15 ml of water, treated with potash, and then extracted with ether. The ether extract was dried over sodium sulfate. Vacuum-distillation of the product gave 3.3 g of substance with b.p. 135-155° at 1 mm. The addition of benzine to this substance gave 0.3 g of starting piperidol (m.p. 114-115°), after which the benzine solution was saturated with dry hydrogen chloride. The obtained hydrochloride of the propionate of the γ-form of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol, after two recrystallizations from a mixture of alcohol and acetone, melted at 188-189°. Weight 1.65 g (30.1 % yield).

Found %: C 69.20, 68.95; H 8.95, 8.78; N 3.88, 3.70; Cl 9.44, 9.28. $C_{21}H_{32}O_2NCl$. Calculated %: C 68.90; H 8.84; N 3.83; Cl 9.69.

b) To a solution of 0.6 g of the γ-form of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 115.5 - 116.5°) in 0.5 ml of dry chloroform was added 0.45 ml of propionyl chloride in drops. The mixture was allowed to stand for several days. The addition of several drops of ether caused the product to crystallize. We obtained 0.25 g of the hydrochloride of the propionate of the γ-from of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4--phenyl-4-piperidol with m.p. 188-189°, failing to depress the melting point when mixed with the preceding specimen.

Propionate of the β-Form of 1-(γ,γ-Dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (IX). A mixture of 1.8 g of the β-form of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 105.5-106.5°), 5 ml of propionic anhydride and 1.5 ml of propionyl chloride was heated at 115-120° for 10 hours. The excess anhydride and chloride were vacuum-distilled, while the residue was treated with absolute ether. The obtained crystalline substance was recrystallized twice from a mixture of alcohol and acetone. We obtained 1.3 g (52%) of the hydrochloride of the propionate of the β-form of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 163-164°.

Found %: C 69.10, 68.66; H 8.69, 8.77; N 4.04, 4.04; Cl 10.58, 10.33. $C_{21}H_{32}O_2NCl$. Calculated %: C 68.90; H 8.84; N 3.83; Cl 9.69.

Propionate of the γ-Form of 1-(γ-Chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (X). A mixture of 2.9 g of the γ-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 110-111°), 5 ml of propionic anhydride and 3 ml of propionyl chloride was heated at 115-120° for 9 hours. After the usual treatment we obtained 1.7 g of the hydrochloride of the propionate of the γ-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl--4-piperidol with m.p. 182.5-183.5° (from a mixture of acetone and anhydrous alcohol). Yield 44 %.

Found %: C 62.42, 62.15; H 7.49, 7.58; N 3.86, 3.76; Cl 18.22, 18.55. $C_{20}H_{29}O_2NCl_2$. Calculated %: C 62.16; H 7.56; N 3.62; Cl 18.37.

Propionate of the β-Form of 1-(γ-Chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (X). A mixture of 2.9 g of the β-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol (m.p. 134-135°), 5 ml of propionic anhydride and 3 ml of propionyl chloride was heated at 115-120° for 8 hours. After the usual treatment we obtained 2.4 g of the hydrochloride of the propionate of the β-form of 1-(γ-chlorocrotyl)-2,5-dimethyl-4-phenyl-4-piperidol with 161-162°. Yield 62 %.

Found %: C 62.19, 61.91; H 7.26, 7.68; N 3.76, 3.63; Cl 18.60, 18.68. $C_{20}H_{29}O_2NCl_2$. Calculated %: C 62.16; H 7.56; N 3.62; Cl 18.37.

SUMMARY

The reaction of phenyllithium with 1-alkenyl-2,5-dimethyl-4-piperidones gave the corresponding 4-phenyl-

-4-piperidols (I - IV) as mixtures of three spatial isomers (of the four theoretically possible), which were separated into the individual compounds by fractional crystallization.

From the γ- and β-forms of the obtained 4-phenyl-4-piperidols we synthesized the propionic esters (VIII-X), which were subjected to pharmacological testing.

In all cases the β-forms of the described propionic esters show a much greater analgesic activity than do the γ-forms. All of the investigated propionic esters are approximately 1/3 as active as promedol and isopromedol.

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SOME PROPERTIES OF 5-HALOFURFURALS

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Earlier we had proposed fully accessible methods for the preparation of the 5-bromo- [1] and 5-iodofurfurals [2]. In the course of further study it was revealed that light exerts a favorable influence on the bromination rate of furfural and especially on the replacement of the bromine atom in the bromofurfural by iodine. Thus, when the bromination of furfural was run in sunlight, with other conditions constant, the yield of the bromofurfural was 60.6 %, while when it was run in the dark the yield dropped to 45.6 %. Replacement of the bromine by iodine is completely nonexistent in the dark, while in the sunlight it goes almost quantitatively.

Next we studied the behavior of the halofurfurals when exposed to heat and the action of alkalies. Here it was found that the bromofurfural, contrary to the literature data that it is relatively unstable to the action of aqueous alkali [3], proved to be exceedingly stable; it is recovered unchanged after boiling for 3 hours with 10 % aqueours NaOH solution.

In contrast to furfural, the halofurfurals (after two recrystallizations from alcohol) remain almost unchanged when stored for a long time. However, if absolutely dry they are much more sensitive to the action of light than if air-dried only [1].

The halofurfurals are volatile, readily distill with steam and other solvents, and sublime when heated above their melting points. The dry and pure bromofurfural distills without decomposition at atmospheric pressure to give a yellowish oil that freezes at 82°. Its b.p. 201-202° (750 mm). The iodofurfural distills at 227° with partial decompsotion.

The halofurfurals are readily soluble in alcohol, methanol, benzene, dichloroethane, chloroform and carbon tetrachloride, and difficultly soluble in petroleum ether and water. The data on the solubility of the halofurfurals in water, alcohol and dichloroethane are presented in the table.

Solubility of Halofurfurals (in Grams) in 100 ml of Solvent at 20° and at the Boiling Point of the Solvent

	Water		Alcohol		Dichloroethane	
	20°	100°	20°	78°	20°	83°
5-Bromofurfural	0.5	2.5	5.0	120.0	3.7	> 360.0
5-Iodofurfural	0	0.5	3.0	40.0	10.0	> 360.0

The same as furfural, the halofurfurals qualitatively react with a solution of aniline in 50 % acetic acid; the bromofurfural gives an orange-red color, while the iodofurfural gives an orange-yellow color.

The habfurfurals readily form various derivatives involving the carbonyl group. The oximes [1, 2] and semicarbazones [2, 3] of the bromo- and iodofurfurals had been obtained by us earlier. In this communication we describe the also readily obtained thiosemicarbazones, 2,4-dinitrophenylhydrazones and bisulfite compounds.

EXPERIMENTAL

The Thiosemicarbazones of the Halofurfurals were obtained by mixing hot solutions of equimolar amounts

of the halofurfural in alcohol and thiosemicarbazide in water and heating the mixture for 30 minutes under reflux on the water bath.

5-Iodofurfural Thiosemicarbazone was obtained as tiny fluffy yellowish needles. M. p. 162-163° (from alcohol). It decomposes at 165° with the evolution of iodine vapors. It quantitatively evolves iodine when treated with concd. HNO_3.

Found %: I 43.12; S 10.52. $C_6H_6ON_3SI$. Calculated %: I 43.03; S 10.85

5-Bromofurfural Thiosemicarbazone was obtained as yellowish crystals with m.p. 196-197° (decompn.) (from alcohol).

Found %: Br 32.03; S 12.67. $C_6H_6ON_3SBr$. Calculated %: Br 32.21; S 12.95.

Furfural Thiosemicarbazone was obtained as white crystals with m.p. 153-154° (from alcohol), and decomposing at 180°.

Found %: S 18.07. $C_6H_7ON_3S$. Calculated %: S 18.46.

The 2,4-Dinitrophenylhydrazones of the Halofurfurals were obtained by boiling a mixture of 0.5 g of the aldehyde and 0.5 g of 2,4-dinitrophenylhydrazine, 2.5 ml of water, 20 ml of alcohol and 2.5 ml of concentrated hydrochloric acid [4]; immediately voluminous, bright-colored precipitates were formed, which were separated, washed with hot 10 % HCl, then with water, and recrystallized from hot benzene.

5-Bromofurfural 2,4-Dinitrophenylhydrazone. Orange-red crystals with m.p. 204-205°.

Found %: Br 22.24. $C_{11}H_7O_5N_4Br$. Calculated %: Br 22.51.

5-Iodofurfural 2,4-Dinitrophenylhydrazone. Brick-red crystals with m.p. 210-211°.

Found %: I 31.03. $C_{11}H_7O_5N_4I$. Calculated %: I 31.32.

The Bisulfite Compounds of the Halofurfurals are easily obtained by shaking an ether solution of the aldehyde with a saturated water solution of sodium bisulfite.

The Bisulfite Compound of 5-Iodofurfural was obtained as white leaflets with m.p. 220°. It quantitatively evolves iodine when treated with concd. HNO_3. The original iodofurfural is obtained when the bisulfite compound is decomposed.

Found %: I 40.63. $C_5H_4O_4SINa$. Calculated %: I 40.95.

The Bisulfite Compound of 5-Bromofurfural was obtained as lustrous white leaflets. The original bromofurfural is obtained when it is decomposed.

Found %: Br 29.98. $C_5H_4O_4SBrNa$. Calculated %: Br 30.39.

SUMMARY

1. It was shown that light catalyzes the bromination of furfural and the replacement of bromine by iodine in 5-bromofuran derivatives.

2. A more detailed study was made of the properties of 5-bromo- and 5-iodofurfurals.

3. Some previously unknown derivatives of the 5-bromo- and 5-iodofurfurals were obtained: the thiosemicarbazones, the 2,4-dinitrophenylhydrazones and the bisulfite compounds.

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STUDY OF ALKALOIDS OF VINCA ERECTA RGL. AND SCHMALH.

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The first to show the presence of an alkaloid in Vinca rosea L. was the Dutch chemist Greshoff [1]. The chemical composition and properties of this alkaloid were not established. Recently the alkaloid vinceine $C_{21}H_{26}O_3N_2$; was isolated from this plant by Paris and Moyse-Mignon [2]; the authors postulated that vinceine is isomeric with yohimbine. The alkaloid δ-yohimbine $C_{21}H_{24}O_3N_2$ [3] was isolated from V. lacea Boj., which earlier had been found in Corynanthe yohimbe Schum. [4] and Rauwolfia serpentina Bent. [5, 6]. Reserpinine $C_{22}H_{26}O_4N_2$, vincamajoridine $C_{22}H_{26}O_4N_2$ and vincamajoreine $C_{21}H_{26-28}O_2N_2$ were isolated from V. major L. [3]. Reserpinine was first found in R. serpentine [6]. From V. pubescens L., found growing in the Soviet Union, A. P. Orekhov and co-workers [7] isolated vinine $C_{19}H_{26}O_4N_2$, pubescine $C_{20}H_{26}O_4N_2$ and a base with m.p. 194-195°. E. S. Zabolotnaya [8] investigated V. minor L., collected near Moscow, and isolated the alkaloid minorine $C_{22}H_{26}O_3N_2$. From V. minor, growing in Switzerland, the alkaloid vincamine and its isomer isovincamine $C_{21}H_{26}O_3N_2$ were isolated [9, 10].

A study of the alkaloids of V. erecta was begun by us. The roots and above ground portion were investigated separately. From the roots we isolated a total of 2.11 % of alkaloids. The latter were separated into a phenolic and nonphenolic fraction. The phenolic fraction represented 1.06 %, and the nonphenolic fraction was 1.05 % (of the weight of dry roots).

A base with m.p. 187.5-188° was isolated from the nonphenolic fraction. It forms a whole series of well-crystallizing monoacidic salts: hydrochloride, hydrobromide, nitrate, perchlorate and picrate. Elementary analysis of the base and of the nitrate leads to the formula $C_{19}H_{22}ON_2$.

Since this alkaloid is not described in the literature, we named it vincanine. The nitrogen in vincanine is tertiary; the alkaloid does not contain methylimido, methoxyl or hydroxyl groups, but does contain one active hydrogen atom. The infrared absorption spectrum of vincanine shows the presence of the NH group (3330 cm^{-1}). Consequently, the nitrogen, not being basic, should be secondary in character. As regards the function of the oxygen, then, judging by the infrared spectrum, it is ketonic in nature (1740 cm^{-1}). This is confirmed by the preparation of the phenylhydrazone, oxime and hydrazone of vincanine. On the basis of the above the deduced formula for vincanine can be depicted as follows:

$$C_{18}H_{21}\ (>NH)\ (>N-)\ (CO)$$

The hydrobromide of a second alkaloid was isolated from the total phenolic bases. Decomposition of the hydrobromide gave a light-yellow base of phenolic character, which we named vincanidine. The latter is also isolated if the mixture of phenolic bases is treated with methyl alcohol. Vincanidine carbonizes at 250-280° without melting, and is difficult to combust. Consequently the nitrate was taken for elementary analysis, and from the analysis the formula $C_{20}H_{24}O_3N_2$ was assigned to the base. Besides the hydrobromide and nitrate we also prepared the hydrochloride, picrate and methiodide. The alkaloid does not contain either methylimido or methoxyl groups.

The roots collected in May contain 1.2%, and those collected in July contain 1.8% total alkaloids. In the early growing period the amount of nonphenolic bases is greater than that of phenolic bases, while towards the end of the growing period their ratio becomes equal. Consequently, the roots of V. erecta contain the greatest amount of alkaloids in the dying period of the above ground portion [11].

Extraction of the above ground portion with dichloroethane gave 0.26 % total alkaloids. After separation we isolated vincanine and a base with m.p. 224-225° from the nonphenolic fraction. Elementary analysis of the

base with m.p. 224-225° shows good agreement with the formula $C_{22}H_{28}O_3N_2$. The alkaloid contains one OCH_3 group and does not contain any NCH_3 groups [12]. The physicochemical properties of this alkaloid show good agreement with the properties of minorine $C_{22}H_{26}O_3N_2$. To make a direct comparison we used the minorine that had been graciously supplied to us by E. S. Zabolotnaya. The mixtures of the bases, as well as of their salts, did not show a melting point depression.

EXPERIMENTAL

Investigation of the Roots of V. erecta *

Isolation of the Alkaloids: Five hundred grams of air-dried and ground roots was moistened with 10 % ammonia, charged into a continuous-extraction apparatus, and extracted with chloroform for 24 hours. The chloroform extract was poured off and shaken repeatedly with 10 % sulfuric acid. The mixture of sulfates of the bases was decomposed with ammonia, and the precipitated bases were extracted with chloroform. The obtained chloroform solution of total alkaloids was washed with 1N KOH. The alkaline solution of phenolic bases was neutralized with 20 % sulfuric acid. The obtained flocculent yellow precipitate of phenolic bases was separated, washed with water, and dried at 50°. We obtained 4.53 g of amorphous yellow powder. The neutral aqueous mother liquor was made alkaline with 25 % ammonia, and the bases were extracted with chloroform. Removal of the solvent by distillation gave 0.75 g of residue as a dark-brown, partially crystalline mass. Total yield of phenolic bases 5.28 g, which represents 1.06 % of the weight of the dry roots.

The chloroform solution of total alkaloids (after separating the phenolic bases) was extracted with 10 % sulfuric acid. The acid solution in the presence of ether was made alkaline with 25 % ammonia. The ether layer was separated. Greenish crystals of technical vincanine, which collected as large rosettes, separated from the ether solution on standing. M.p. 178-180°. Yield 1.8 g. After removing the crystals the mother liquor was evaporated to small volume, here an additional 1.6 g of vincanine was obtained as needlelike crystals. The total yield of technical vincanine was 3.5 g, which represents 0.7 % of the weight of dry roots. Evaporation of the mother liquor gave 1.76 g of a brown tarry mass. The total yield of nonphenolic bases was 5.26 g (1.05 %).

Vincanine. The technical vincanine was recrystallized from methyl alcohol. Plates with m.p. 187.5-188° were obtained. $[\alpha]_D^{17}$ -992° (c = 1.390; methanol).

Found %: C 77.65; H 7.11; N 9.64; H (active) 0.3663. Eqv. 294. M 302. $C_{19}H_{22}ON_2$. Calculated %: C 77.48; H 7.54; N 9.52; H (active) 0.3447. Eqv. and M 294.36.

Vincanine Hydrochloride was formed by rubbing the free base with 15 % hydrochloric acid. After recrystallization from hot water it was obtained as needle crystals with a greenish tinge. M. p. 110-111°. Vacuum-drying revealed that vincanine hydrochloride contains one molecule of crystallization water. When recrystallized from alcohol the anydrous hydrochloride is obtained with m.p. 211-212°; readily soluble in methy alcohol, and difficultly soluble in ethyl alcohol and in water. It darkens when exposed to the light for a long time. It remains unchanged in the dark. $[\alpha]_D^{20}$ - 932.8° (c = 1.163; methanol).

Found %: Cl 10.46. $C_{19}H_{22}ON_2 \cdot HCl$. Calculated %: Cl 10.8.

Vincanine Nitrate is formed when nitric acid is added to a saturated alcohol solution of the free base. M.p.193-194°(with decompn.) (from alcohol).

Found %: C 64.44; H 6.13; N 11.38. $C_{19}H_{22}ON_2 \cdot HNO_3$. Calculated %: C 63.92; H 6.46; N 11.72.

Vincanine Hydrobromide is obtained as a precipitate when strong hydrobromic acid is added to an alcohol solution of the free base. Tiny needle crystals with a slight greenish tinge. M. p. 225-227° (from alcohol).

Vincanine Perchlorate. To a hydrochloric acid solution of the free base in anhydrous alcohol was added a water solution of ammonium perchlorate. Coarse needle crystals, which collected in rosettes, began to deposit from the solution after a day. M. p. 206-207° (from alcohol).

Vincanine Picrate is formed when alcohol solutions of the free base and picric acid are mixed. M.p. 207--208° (from alcohol).

* The roots were collected by E. E. Korotkov in the Fergana valley (near the village of Khodzha-Ata) at the time that the above ground portion was completely dead (September 19 - 22, 1949).

Vincanine Methiodide. To a solution of 0.5 g of the free base in methyl alcohol was added 0.5 ml of methyl iodide. The mixture evolved heat. Fine needle crystals of the methiodide (0.5 g) separated on standing. M. p. 280-282° (from methanol).

Found %: I 29.67. $C_{19}H_{22}ON_2 \cdot CH_3I$ Calculated %: I 29.26.

Vincanine Phenylhydrazone. To a solution of 1 g of vincanine hydrochloride in 60 ml of hot water was added 0.45 g of phenylhydrazine hydrochloride. The mixture was heated on the water bath for 1 hour. Here the vincanine phenylhydrazone hydrochloride was obtained as a slightly yellowish finely crystalline precipitate (1 g). M. p. 285-286° (from aqueous alcohol). $[\alpha]_D^{19}$ - 147.29° (c = 1.962; methanol). A solution of 0.5 g of vincanine phenylhydrazone hydrochloride in 50 ml of water was made alkaline with 10 % ammonia solution. The obtained precipitate of vincanine phenylhydrazone was extracted with ether. Removal of the ether from the ether extract by distillation gave the vincanine phenylhydrazone as white crystals with m.p. 183-184°. $[\alpha]_D^{19}$ -192.36° (c = = 1.258; methanol).

Found %: N 14.58. $C_{25}H_{28}N_4$. Calculated %: N 14.57.

Vincanine Hydrazone. Water solutions of vincanine hydrochloride (0.2 g) and hydrazine sulfate (0.1 g) were mixed and the mixture heated on the water bath for 30 minutes. The solution after cooling was made alkaline with ammonia, and the obtained precipitate was extracted with ether. Evaporation of the ether extract gave 0.2 g of vincanine hydrazone with m.p. 240-241°.

Vincanine Oxime was obtained in the same manner as vincanine hydrazone, using vincanine hydrochloride (0.6 g) and hydroxylamine sulfate (0.25 g). M. p. 110-112° (from ether).

Vincanidine. Five grams of total phenolic bases were mixed with acetone and the mixture was treated with strong hydrobromic acid. The obtained vincanidine hydrobromide (2 g) had m.p. 169-170° (from water). $[\alpha]_D^{20}$ - - 672.8° (c = 1.556; methanol). One gram of the hydrobromide was dissolved in 20 ml of water and made alkaline with 10 % ammonia. The obtained precipitate (0.7 g) was suction-filtered and washed with water. After recrystallization from methanol (1 : 50) the compound was obtained as light-yellow, fine needle crystals. The free base carbonizes at 250-280° without melting. The free base is difficultly soluble in ethyl and methyl alcohols, acetone, chloroform and benzene. It is readily soluble in pyridine and alkalies.

Vincanidine Nitrate. To a mixture of 0.5 g of the free base and 5 ml of water was added with vigorous stirring a 10 % nitric acid solution until acid to congo. Here the free base was observed to go into solution, and then light-yellow needle crystals began to deposit immediately. M. p. 142-142.5° (from alcohol).

Found %: C 59.35; H 5.98; N 10.48; $C_{20}H_{24}O_3N_2 \cdot HNO_3$. Calculated %: C 59.5; H 6.22; N 10.42.

Vincanidine Hydrochloride. Obtained in the same manner as the nitrate, i.e. by the addition of hydrochloric acid to the free base. The hydrochloride was obtained as fine yellow needle crystals with m.p. 175° (from water).

Vincanidine Picrate. Obtained by mixing alcohol solutions of the free base and picric acid. M. p. 220-221° (from alcohol).

Vincanidine Methiodide. To a solution of 0.2 g of the free base in 10 ml of methanol was added 1 ml of methyl iodide. This resulted in the deposition of the fine lamellar crystals (0.2 g). M.p. 312-315° (from methanol).

Found %: I 30.24. $C_{20}H_{24}O_3N_2 \cdot CH_3I$ Calculated %: I 29.04.

Investigation of the Above Ground Portion of V. erecta

From 48 kg of above ground portion, collected at the stage of flowering and formation of fruit (May 16-19, 1950), by the usual dichloroethane extraction (6 decantations) we isolated 128 g of alkaloids (0.26 %), which were separated into a phenolic and a nonphenolic fraction. From the ether extract of the nonphenolic bases we obtained a small amount of vincanine and a base with m.p. 224-225° (5 g).

Found %: C 71.90; H 7.46; N 7.74; OCH_3 8.85. $C_{22}H_{28}O_3N_2$. Calculated %: C 71.79; H 7.65; N 7.65; OCH_3 8.42.

The base is readily soluble in chloroform, and difficultly soluble in ethyl ether and acetone. Its hydrochloride

with m.p. 226-227°, nitrate with m.p. 214-215°, picrate with m.p. 202-203° and methiodide with m.p. 214-215° were obtained in the usual manner.

SUMMARY

1. The roots of Vinca erecta Rgl. and Schmalh. contain the greatest amount of alkaloids (2.11%) during the dying period of the above ground portion of the plant. Two new alkaloids – vincanine and vincanidine – were obtained from the roots of V. erecta.

2. Vincanine and the previously known minorine were isolated from the above ground portion of V. erecta.

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OPEN TO DISCUSSION

IN CONNECTION WITH THE ARTICLE BY V. F. BOIKO "A STUDY IN THE FIELD OF BASIC CHLORIDES OF IRON"

G. B. Fridman

V. F. Boiko [1] has studied the composition of the product of the hydrolysis of ferric chloride using the fourth component method [2]. According to his data, the composition of the hydrolysis product of ferric chloride changes with aging of the specimen, thus: after 6 months it corresponds to the formula $FeCl_3 \cdot 7Fe_2O_3 \cdot 21H_2O$ and after 18 months to the formula $FeCl_3 \cdot 8Fe_2O_3 \cdot 16H_2O$.

The reduction in the degree of hydration of a colloid on aging is quite regular and has been observed more than once by a number of workers. As far as the reduction in the ratio $Fe_2O_3/FeCl_3$ with aging of the specimen, observed by V. F. Boiko, is concerned, it is the result of the hydrolysis of the oxychloride $FeCl_3 \cdot 7Fe_2O_3 \cdot 21H_2O$. The tendency of the oxychloride to undergo hydrolysis in the absence of $FeCl_3$ has been pointed out in the literature: according to data obtained in a study of the systems $Fe_2O_3-H_2O-FeCl_3-CaCl_2$ and $Fe_2O_3-H_2O-FeCl_3-Ba(NO_3)_2$ [3] iron oxychloride is stable only in contact with fairly concentrated $FeCl_3$ solutions; on washing, for example, with $Ba(NO_3)_2$ solution, it is completely hydrolyzed and converted to the hydrate of composition $2Fe_2O_3 \cdot 3H_2O$. This tendency of iron oxychloride to undergo hydrolysis has not been taken into account by V. F. Boiko, who studied the system $Fe_2O_3-H_2O-FeCl_3-CaCl_2$ in the absence of $FeCl_3$ in the liquid phase and who has permitted washing of the oxychloride with calcium chloride solution, which although containing a common ion with the oxychloride, does not, as V. F. Boiko's experiments show, completely suppress the hydrolysis.

In addition, V. F. Boiko has committed another error in assuming that, in the $Fe_2O_3-H_2O-FeCl_3-CaCl_2$ system studied earlier [3], negative adsorption of ferric chloride takes place, which, (as V. F. Boiko writes) "...should lead to low results in the determination of the ferric chloride." This assertion made by V. F. Boiko is without foundation. As is well known, one can only speak of negative adsorption when the concentration of the adsorptive on the suface of the phase boundary is less than in the bulk of the phase. Since the fourth component ($CaCl_2$), blocking the surface of the solid phase, displaces from it all other adsorbed components ($FeCl_3$ and H_2O), it is natural that the $FeCl_3$ concentration on the suface of the solid phase is zero. Since the liquid phase contains $FeCl_3$, it is of course possible, if one so desires, to call the concentration of $FeCl_3$ in the liquid phase (i.e. the difference "concentration of $FeCl_3$ in the liquid phase minus zero") negative adsorption, but it is quite obvious that such "negative adsorption" can in no way "lead to low results in the determination of the ferric chloride" and that no corrections for such "negative adsorption" are required.

From what has been said it follows that 1) the error assumed to be based on the application of the fourth component method and detected by V. F. Boiko is imaginary, and the discrepancy between the results of the study of iron oxychloride obtained by G. B. Fridman and the results obtained by V. F. Boiko is explained by the fact that in his work V. F. Boiko has not taken the steps necessary to prevent the hydrolysis of the basic salt (the introduction of $FeCl_3$ to the liquid phase). 2) V. F. Boiko has no grounds for changing the description "fourth component method", which is established in the literature, to the other description "indifferent component method."

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LETTERS TO THE EDITOR

I

Our article "The Synthesis and Properties of Sulfamethine – a New Antituberculosis Preparation" was published in the "Journal of General Chemistry" [26, 168 (1956)]*. We gave the trade name "sulfamethine" to the azomethine derivative of 4,4'-diaminodiphenyl sulfone. It later became known that a sulfamide preparation had previously been issued in the German Democratic Republic under the same trade name. In view of this the USSR Ministry of Public Health have changed the name of the antituberculosis preparation "sulfamethine" to "sulfonine".

We request publication of this letter for the information of workers interested in our preparation.

Per Professor R. P. Veltman

Received July 4, 1957.

II

Due to the authors' oversight, the article by M. Ya. Fioshin, G. P. Girinaya and V. P. Mamaev published in the "Journal of General Chemistry" [26, 2311 (1956)]* gave incorrect values for the melting points of benzaldehyde methoxyphenylhydrazones.

The melting point of benzaldehyde p-methoxyphenylhydrazone is 123-124° and the melting point of benzaldehyde o-methoxyphenylhydrazone is 88-89°.

M. Ya. Fioshin

V. P. Mamaev

*Original Russian pagination. See C. B. Translation.

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